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VOL. 172 PART I

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# JOURNAL

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# ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| Å. | Ångstrom unit(s) = $1 \times 10^{-10}$ m. |
| A.C. | air-cooled; alternating current |
| A.H. | air-hardened |
| amp. | ampère(s) |
| amp.hr. | ampère-hour(s) |
| approx. | approximately |
| at.-% | atomic per cent |
| at.wt. | atomic weight |
| atm. | atmosphere(s) (pressure) |
| A.W.G. | American wire-gauge |
| ° Bé. | Baumé (degree) |
| b.h.p. | brake horse-power |
| B. & S. | Brown and Sharpe (gauge) |
| B.o.T. | Board of Trade |
| b.p. | boiling point |
| B.T.U. | Board of Trade unit(s) |
| B.Th.U. | British thermal unit(s) |
| B.W.G. | Birmingham wire-gauge |
| ° C. | centigrade; Celsius (degree) |
| cal. | calorie(s) |
| c.c. | cubic centimetre(s) |
| c.d. | current density |
| c.g.s. | centimetre-gramme-second unit(s) |
| cm. | centimetre(s) |
| coeff. | coefficient(s) |
| conc. | concentrated |
| const. | constant(s) |
| cu. | cubic |
| cwt. | hundredweight(s) |
| D.C. | direct current |
| dia. | diameter |
| dil. | dilute |
| dm. | decimetre(s) |
| e.m.f. | electromotive force |
| e.v. | electron volt(s) |
| ° F. | Fahrenheit (degree) |
| ft. | foot, feet |
| ft.lb. | foot-pound(s) |
| g. | gramme(s) |
| gal. | gallon(s) |
| H.F. | high-frequency |
| h.p. | horse-power |
| h.p.hr. | horse-power-hour(s) |
| hr. | hour(s) |
| in. | inch(es) |
| in.lb. | inch-pound(s) |
| I.S.W.G. | Imperial standard wire-gauge |
| ° K. | absolute temperature (Kelvin scale) |
| kg. | kilogramme(s) |
| kg.cal. | kilogramme-calorie(s) |
| kg.m. | kilogramme-metre(s) |
| km. | kilometre(s) |
| kV. | kilovolt(s) |
| kVA. | kilovolt-ampère(s) |
| kW. | kilowatt(s) |
| kWh. | kilowatt-hour(s) |
| kX. | crystal Ångstrom(s) = 1000 Siegbahn X-units |

| | |
|---|---|
| l. | litre(s) |
| lb. | pound(s) |
| L.F. | low-frequency |
| *M* | molar (solution) |
| m. | metre(s) |
| m.amp. | milliampère(s) |
| max. | maximum |
| mg. | milligramme(s) |
| min. | minimum; minute(s) |
| ml. | millilitre(s) |
| mm. | millimetre(s) |
| m.m.f. | magnetomotive force |
| m.p. | melting point |
| mV. | millivolt(s) |
| mμ | millimicron = $1 \times 10^{-9}$ m. = 10 Å. |
| *N* | normal (solution) |
| N.T.P. | normal temperature and pressure |
| O.H. | open-hearth; oil-hardened |
| O.Q. | oil-quenched |
| oz. | ounce(s) |
| p.d. | potential difference |
| *p*H | hydrogen-ion concentration |
| p.p.m. | parts per million |
| r.p.m. | revolutions per minute |
| sec. | second(s) |
| sp.gr. | specific gravity |
| sq. | square |
| S.W.G. | standard wire-gauge |
| T. | tempered |
| temp. | temperature |
| V. | volt(s) |
| VA. | volt-ampère(s) |
| W. | watt(s) |
| Wh. | watt-hour(s) |
| W.G. | water-gauge |
| W.Q. | water-quenched |
| wt. | weight |
| wt.-% | weight per cent |
| yd. | yard(s) |
| μ | micron(s) = $1 \times 10^{-6}$ m. |
| μg. | microgramme(s) = $1 \times 10^{-6}$ g. |
| μμ | 1 millionth micron = $1 \times 10^{-12}$ m. = 0·01 Å. |
| Ω | ohm(s) |
| ° | degree (arc or temperature) |
| ′ | minute of arc; foot (feet) |
| ″ | second of arc; inch(es) |
| $<$ | less than |
| $>$ | greater than |
| $\not<$ | not less than |
| $\not>$ | not greater than |
| $\leqslant$ | equal to or less than |
| $\geqslant$ | equal to or greater than |
| $\neq$ | not equal to |
| $\equiv$ | identically equal to |
| $\simeq$ | approximately equal to |
| $\propto$ | proportional to |

Unless otherwise stated above, the symbols given in the following British Standards are used in the *Journal*:
Chemical, Thermodynamical, and Physico-chemical quantities: B.S. 813; Engineering units: B.S. 560.

## N. C. LAKE

NORMAN C. LAKE was born at Hanley, North Staffordshire, in 1905, and was educated at Newcastle-under-Lyme and Longton and at the North Staffordshire Technical College, Stoke-on-Trent.

He served his apprenticeship in the machine and fitting shops and drawing office of The Shelton Iron, Steel and Coal Company, Limited, and early in 1928 he joined Daniel Adamson and Company, Limited, Dukinfield, as a junior draughtsman. Later in the same year he went to International Combustion Limited, Derby, and in 1929 he joined I.C.I. (Metals) Limited, Birmingham, as a draughtsman, being engaged on the layout of rolling mills for the production of non-ferrous metals. In 1931 he was appointed Assistant Chief Draughtsman and was responsible, under the Chief Engineer, for the design of specialized equipment including rolling mills and extrusion presses.

In 1936 Mr. Lake was appointed Manager of the newly-formed Steelworks Plant Department of Head, Wrightson and Company, Limited, Thornaby-on-Tees. In 1945 the Company acquired an engineering works in Middlesbrough, which was modernized and equipped with new machine tools for the production of rolling mill equipment. When the Steelworks Plant Department became The Head Wrightson Machine Company, Limited, in 1946, Mr. Lake was appointed Director and General Manager. During his connection with the Head Wrightson Group, he has been responsible for many very large home and export contracts for equipment for the production of steel and non-ferrous metals.

Mr. Lake was for many years a member of the Rolling-Mill Research Sub-Committee of the Iron and Steel Industrial Research Council, as representative of the Steel Works Plant Association, of which he is Chairman. He recently became a member of the Drawing Committee of the British Iron and Steel Research Association. He became a member of the Cleveland Institution of Engineers in 1936 and a member of the Council in 1945, and is President for the current session. He was elected a Member of The Iron and Steel Institute in 1936, and has taken a keen interest in the Iron and Steel Engineers' Group since its inception.

*Navana Vandyk*

**N. C. Lake**
**Honorary Member of Council**

IRON AND STEEL
INSTITUTE PAPERS

PLANT DESIGN · MANUFACTURE · RESEARCH · DEVELOPMENT

ANDREW CARNEGIE SCHOLARSHIP REPORT

# Phase Equilibrium Investigation of the $Na_2O$–$P_2O_5$–$SiO_2$ Ternary System

*By E. T. Turkdogan, Ph.D., M.Met., and W. R. Maddocks, Ph.D.*

SYNOPSIS

This paper is regarded as an introduction to the investigation of the phase distribution in sodium oxide-bearing slags. The effect on the removal of phosphorus has recently been studied by the same authors. The present findings reveal that this is a eutectiferous system with little or no solid solubility. The systems have been established by thermal analysis, specific gravity, and microscopic and X-ray determination. The binary and the ternary phase-equilibrium diagrams produced are the conclusions of the present investigation, which has been conducted by the aforementioned methods. On the $Na_2O$–$SiO_2$ binary side, there are two stable compounds and one peritectic compound. On the $Na_2O$–$P_2O_5$ binary side, there are three stable compounds. Within the entire system, one stable and two peritectic ternary compounds exist. Finally, there is an indication of an immiscibility gap in the melts rich in phosphorus pentoxide and silica. No attempt has been made to correlate the phase distribution in this system to the effect of soda-slags on dephosphorization.

In dealing with the removal of phosphorus by soda-slags, the authors' previous findings[1] were confined stringently to the variation by slag composition and temperature of the degree of dephosphorization. The effect of the former was noted to be more prominent. To support the theoretical arguments on the dephosphorizing reactions, an endeavour was made to correlate the variation of slag density with its composition. This attempt substantiated the assumption of the entity of the slag-forming constituents. The use of the additive and constitutive property of specific volume of a substance to determine the quantities and/or presence of its constituents is rather limited and is regarded as an indirect method. To advance the theory of phosphorus elimination by soda-slags, more must be known about the characteristics of the compounds that may constitute these slags. X-ray and microscopic examinations of these slags, which consist of ten oxides plus various complex compounds, were found to be very unsatisfactory because of the absence of reliable data on their physical and chemical properties. To investigate the distribution of phases in soda-slags, it is therefore essential to know the phase-equilibrium diagrams of simple systems whose components take part in the constitution of these experimental slags.

For the present, only a small area in the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system has been investigated.

## EXPERIMENTS

A standard molybdenum wire-wound furnace was used.

### Synthetic Slags

A mixture of 530 g. of sodium carbonate (310 g. of sodium oxide) and 600 g. of Dutch sand (99·86% $SiO_2$) was placed in a graphite pot with lid, and fused in a gas furnace at 1000° C. After being soaked at this temperature for three hours, it was cooled slowly in the furnace. The analysis of a representative sample was :

| $SiO_2$, % | $Na_2O$, % | $Fe_2O_3$, % | C, % | $CO_2$, % | Total |
|---|---|---|---|---|---|
| 68·91 | 30·63 | 0·02 | 0·01 | 0·34 | 99·91 |

The intended composition of this silicate was that of sodium di-silicate, 65·96% $SiO_2$ and 34·04% $Na_2O$. Only about 3·4% of $Na_2O$ had been lost during the melt. The contamination of the melt by carbon and ferric oxide is significantly low. The base silicate was

The final report, received 24th May, 1951, on research carried out with the aid of a grant from the Andrew Carnegie Research Fund. Revised MS received 26th February, 1952.

Dr. Turkdogan is head of the Physical Chemistry Section of the Chemistry Department of the British Iron and Steel Research Association, and Dr. Maddocks is Senior Lecturer in Ferrous Metallurgy, University of Sheffield.

**Table I**

**COMPOSITION OF SLAGS BEFORE AND AFTER MELTING**

| Melt No. | $Na_2O$, % | $P_2O_5$,% | $SiO_2$,% |
|---|---|---|---|
| (*4NPS*) 11 | | | |
| Before the melt | 55·30 | 32·40 | 12·30 |
| After ,, ,, | 55·16 | 32·10 | 12·74 |
| (*4NP2S*) 17 | | | |
| Before the melt | 47·40 | 24·70 | 27·90 |
| After ,, ,, | 47·08 | 24·92 | 28·00 |
| (*1E*) 4 | | | |
| Before the melt | 49·30 | 7·70 | 43·00 |
| After ,, ,, | 49·52 | 7·92 | 42·56 |
| (*2E*) 6 | | | |
| Before the melt | 46·75 | 40·75 | 12·50 |
| After ,, ,, | 46·70 | 41·00 | 12·30 |

then crushed and ground to pass through a 100-mesh sieve ; it was invariably used in the preparation of the $Na_2O$–$P_2O_5$–$SiO_2$ slags.

After being mixed well in a glass jar, 20–25 g. of the mixture was placed in a platinum crucible and fused in a gas muffle at 1100° C. When the pre-sintering operation was complete the slag was ground, mixed, and refired at 1100° C. Then the platinum crucible containing the slag was put into the high-temperature furnace, where the slag was soaked for 12 hr. at about 100° C. above its melting point. After the molten slag had been stirred with a platinum rod, a 13% Rh–Pt/Pt thermocouple was immersed into the bath and thermal analysis was made.

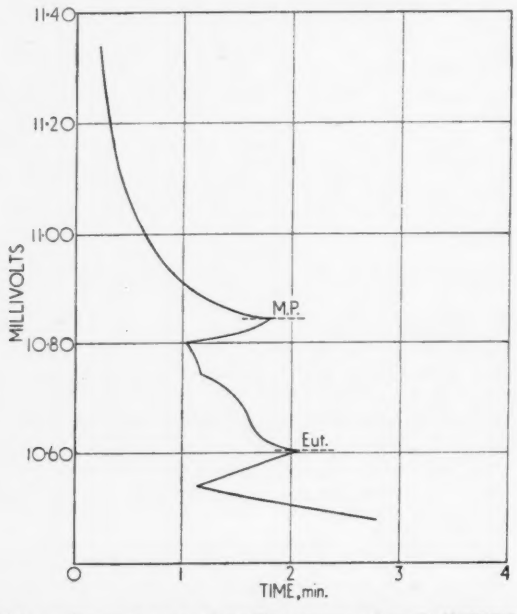



**Fig. 1—Inverse rate of cooling curve of melt (*4NPS*)5**

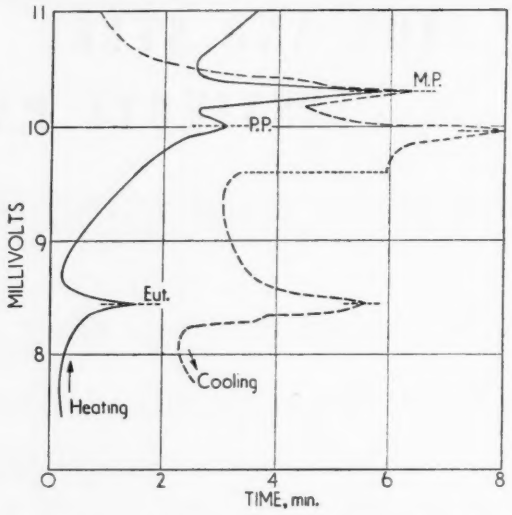



**Fig. 2—Inverse rate of heating and cooling curves of melt (*4NP2S*)8**

To ensure a quick response to the change in the temperature of the bath, the immersed part of the thermocouple was left naked. Although there was no contamination of the thermocouple by the slag, the hot junction was renewed after each melt.

This procedure for preparing the synthetic slags was most satisfactory, and no difficulty was experienced in obtaining a slag of a required composition. The difference in composition before and after each melt was negligible, as shown in Table I. Although the slag compositions were almost identical before and after the melt, each slag was analysed after being melted.

### Thermal Analysis

Under certain conditions, heating and cooling curves were quite satisfactory and arrests could be reproduced reasonably well (within $\pm 5°$ C. throughout the system). Slags containing high percentages of $SiO_2$ or $P_2O_5$ are apt to be glassy when cooled at rates greater than 1° C./min. The extent of the formation of glass appears to be affected by the initial temperatures of the slag, by its composition, and by the rate of cooling.

Figure 1 shows the inverse rate of cooling curve for the melt containing 53·0% of $Na_2O$, 16·5% of $P_2O_5$, and 30·5% of $SiO_2$. The rate of cooling was 0·3° C./min., and the arrests were very clearly defined. In all experiments, the peak of the arrest was taken as the phase-change temperature.

Figure 2 shows curves for the melt containing 40·9% of $Na_2O$, 12·6% of $P_2O_5$, and 46·5% of $SiO_2$. There are three arrest points, corresponding to melting, peritectic, and eutectic points. The arrest temperatures on heating and cooling, at an average rate of 0·3° C./min., are almost identical.

The curve in Fig. 3 is for the melt containing 46·8% of $Na_2O$, 43·0% of $P_2O_5$, and 10·2% of $SiO_2$. The average rate of cooling was 0·56° C./min., and sharp arrest points were obtained.

At a given rate of heating or cooling, the phase transformations generally became more sluggish as the composition of the melts approached the $Na_2O$–$SiO_2$ binary side. Beyond the eutectic compositions, less than 5 mole-% from the $Na_2O$–$SiO_2$ binary side, continuous cooling even at a rate of 0·2° C./min. was not slow enough to cause crystallization. Similar cases were experienced in melts whose compositions lay near the meta-phosphate phase. Under these conditions, the melts were soaked at temperatures below their melting points until crystals were formed, and were then cooled very slowly below their solidification temperatures. The crystallized mass was then heated at 0·3–0·2° C./min. so that the phase-change temperatures could be found.

In melts that contained high percentages of sodium ortho- and/or pyro-phosphates, the rate of cooling could be increased to as much as 5·0° C./min. Curves for sodium ortho-phosphate (4·0° C./min.) are drawn in Fig. 4. This compound melts at 1583° C., and on cooling there appears to be a phase transformation at 1474° C. Undercooling was particularly noticeable in melts containing sodium pyro-phosphate.

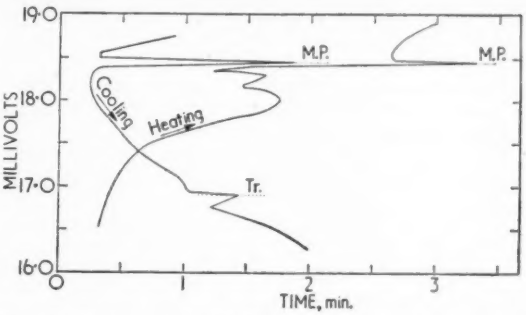



**Fig. 4—Inverse rate of heating and cooling curves of melt (*NP*)1 ($3Na_2O.P_2O_5$)**

#### Specific Gravity Determinations

The specific gravities of all the slags were determined by the method previously described.[1] The density determinations were reproducible to a high degree of accuracy, and the mean deviation for the duplicate figures was as close as ± 0·002 g./c.c., which in terms of specific volume was about ± 0·0004 c.c./g. Accuracy of this order was essential because the specific gravities of the slags in the part of the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system investigated differed by such small amounts. The maximum difference between the specific volumes of the present experimental slags was about 0·06 c.c./g.

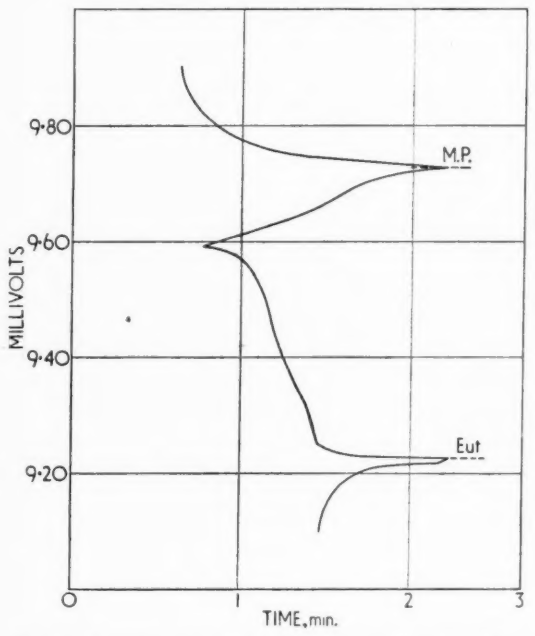



**Fig. 3—Inverse rate of cooling curve of melt (2*E*)7**

#### Petrological and X-Ray Examinations

Metallographic examination of the slags under reflected light was unsuccessful, but petrological examination revealed information useful in the construction of the ternary system.

X-ray patterns were obtained by means of a Philips X-ray set using the Debye-Scherrer-type powder camera (114·59 mm. effective dia.). The X-ray unit was fitted with an iron target, and by using a manganese filter a $K_\alpha$ monochromatic beam of 1·935 Å. wavelength was obtained. Although these slags gave faint diffraction lines, satisfactory qualitative observations could be made. X-ray patterns are omitted because of the difficulty in reproducing them.

## INTERPRETATION OF THE EXPERIMENTAL RESULTS

Melts were made along those sections that were probable two-phase regions over the part of the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system to be studied. Along these sections the number of arrests in any single melt did not exceed three, the first being the melting point, and the second and third corresponding to invariable points that were clearly defined by the constancy of the temperatures. Furthermore, the liquidus curves between the two stable compounds that were the components of the section sloped downwards to meet at the eutectic invariant. There appeared to be little or no solid solubility. This fact was confirmed by the examination of the specific-volume data.

The specific volume of a substance is both additive and constitutive in character. Thus, if the specific volumes of the mixtures in eutectiferous binary systems are plotted against their compositions, the points will fall on the straight line that joins the specific volumes of the two components of the system. A binary system may sometimes contain stable and/or unstable compounds with or without solubilities, and so any solid-phase change between the original components of the system will cause discontinuity in the specific-volume curve. In a eutectiferous binary system, where some intermediate compounds occur without solid solubility, each break in the specific-volume straight line may be considered to indicate

the composition of a compound, but no correlation can be expected between the specific volume of an intermediate compound and those of the original components of the system. The intermediate compounds usually have smaller (although sometimes larger) specific volumes than their components.

The stable compounds occurring on the $Na_2O$–$P_2O_5$ and $Na_2O$–$SiO_2$ binary sides are the major component phases in the investigated area of the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system. To identify them under the microscope, the optical properties of the original components must be known. The eutectics in these artificial slags do not show the same characteristics as those occurring in metallic systems, but the phases, whose optical properties have already been found, can easily be recognized in binary and ternary eutectics. Because of the similarity of the refractive indices of these slags, the determinations have been limited to those of the stable compounds.

The X-ray examination of the slags was intended to confirm the findings by other methods, and no attempt was made to take quantitative measurements. The first notable feature was the absence of diffuse lines, which indicates that the slags were crystalline. Furthermore, no change in the position of the lines was observed, which is taken as an indication of the absence of solid solubility. In all cases, the eutectics show two or three sets of lines that belong to the components of the system.

The system $Na_2O$–$P_2O_5$–$SiO_2$ has been constructed from the combined results of thermal analysis, specific volume, refractive index, and petrological and X-ray examinations. The first three provide quantitative measurements, and the last two are confirmative. All results were compatible, although it was not always possible to determine the crystal system, and the optical and other fundamental properties.

## BINARY SYSTEMS

### Sodium Oxide–Silica Binary System

The phase-equilibrium diagram of the $Na_2O$–$SiO_2$ binary system has been thoroughly investigated by Morey and Bowen[2] and Kracek.[3] The diagram is reproduced in Fig. 5. The invariant points in this system are given in Table II*a*.

The binary compounds di-silicate ($Na_2O.2SiO_2$) and meta-silicate ($Na_2O.SiO_2$) are stable at their melting points. A third compound, ortho-silicate ($2Na_2O.SiO_2$), has an incongruent melting point, *i.e.*, it is a peritectic compound resulting from the reaction between $Na_2O$ crystals and liquid (41·5 mole-% $SiO_2$) at 1118° C. Because of the experimental difficulties, the $Na_2O$ liquidus is not known.

Sodium meta-silicate melts at 1089° C. according to Kracek, whereas the authors' thermal analysis shows it to be 1088° C. The liquidus curve of the meta-silicate on the ortho-silicate side ends at the $2Na_2O.SiO_2/Na_2O.SiO_2$ eutectic, at 43·9 mole-% $SiO_2$ and 1022° C.

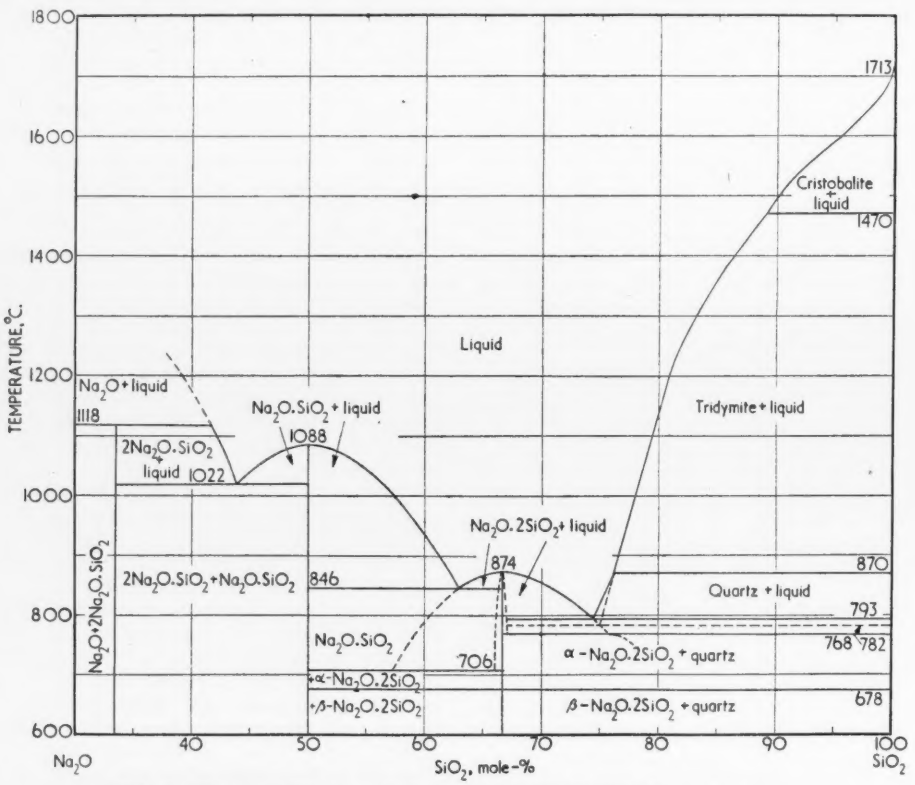



**Fig. 5—Phase-equilibrium diagram of the $Na_2O$–$SiO_2$ binary system**

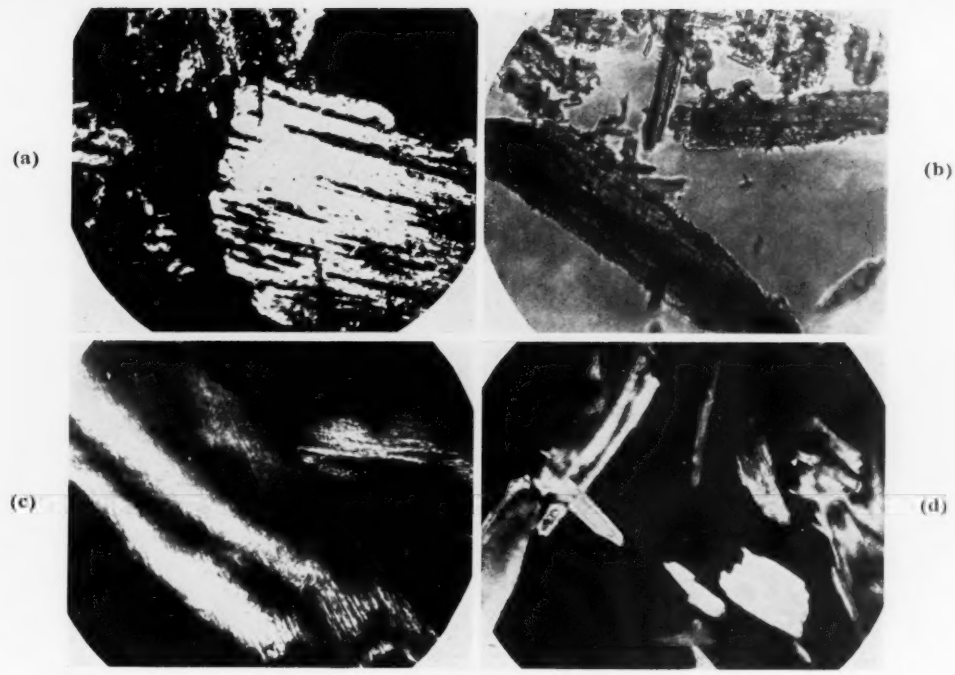



**Fig. 6**—Sodium meta-silicate : (*a*) Micro-slice, showing cleavage (between crossed nicols × 100) ; (*b*) fragments in clove oil, showing form and cleavage (in ordinary light × 400) ; (*c*) and (*d*) fragments in clove oil, showing polarization colour-bands and cleavage (between crossed nicols × 400)

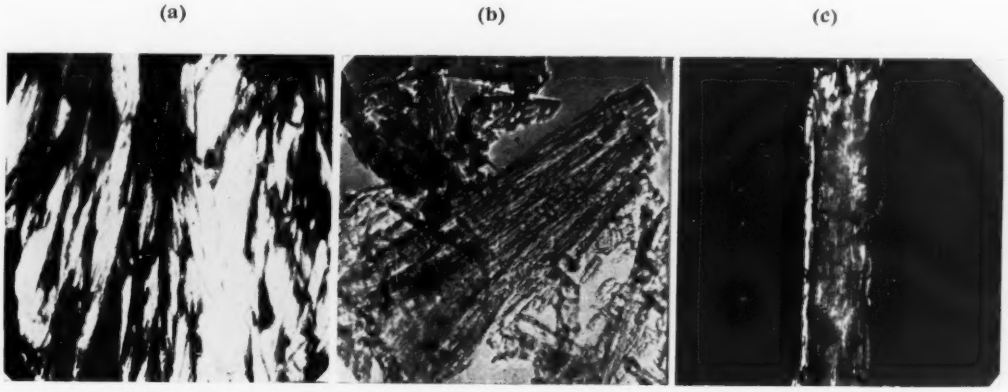
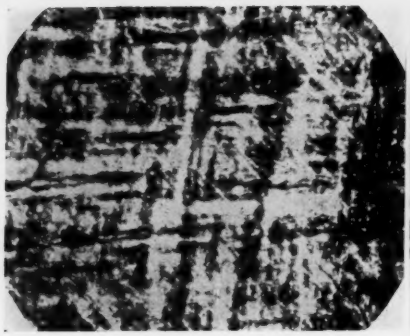
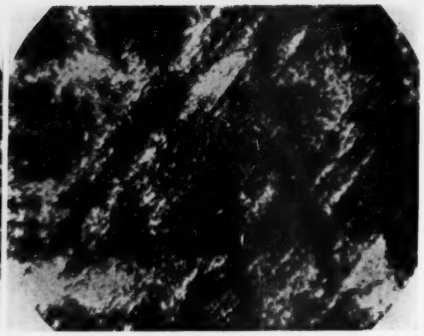



**Fig. 7**—Sodium di-silicate : (*a*) Micro-slice, showing fibrous structure (between crossed nicols × 100) ; (*b*) fragments in clove oil, showing form and cleavage (in ordinary light × 400) ; (*c*) fragments in clove oil showing form (between crossed nicols × 400)

(a)





(b)

Fig. 8—Micro-slice of tri-basic sodium phosphate, showing $\beta$-phase along (111) planes of $\alpha$-phase (between crossed nicols) ; (*a*) × 100 ; (*b*) × 400

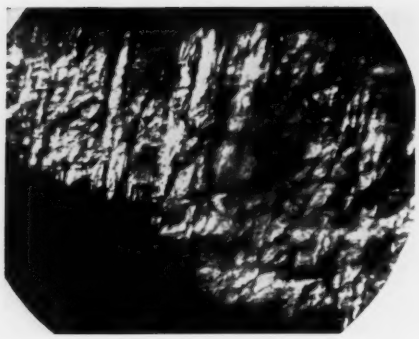


Fig. 9—Fragment of $\beta$-$3Na_2O.P_2O_5$ in clove oil, showing lamellar twinning (between crossed nicols) × 400

Fig. 10—Fragment of sodium pyrophosphate in clove oil ; basal section showing the cleavage parallel to the *c*-axis (in ordinary light) × 400

(a) (b) (c)

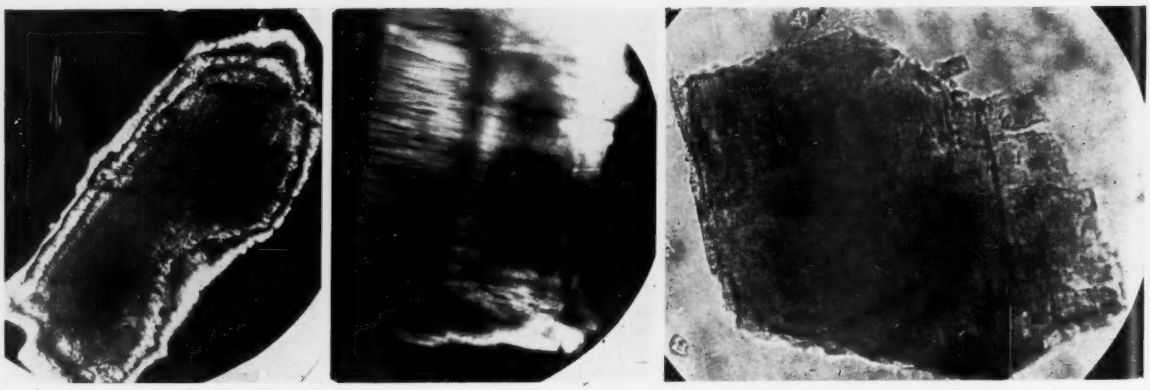


Fig. 11—Fragments of sodium meta-phosphate in clove oil : (*a*) Section parallel to the *c*-axis, showing the rhombic cleavage planes which make 30° with extinction ; (*b*) section along a rhombic cleavage, showing the cleavage planes parallel to the *c*-axis ; (*c*) basal section, showing the outlines of a hexagon. ((a) and (*b*) between crossed nicols, (*c*) in ordinary light) × 400

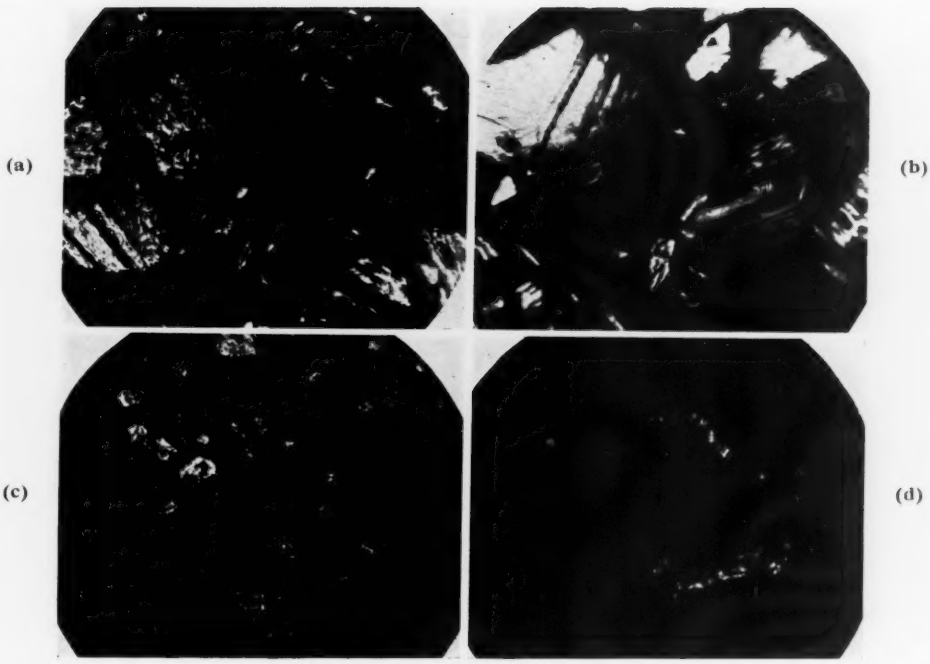



**Fig. 12—Fragments of slags in the $2Na_2O.P_2O_5$—$9Na_2O.2P_2O_5.6SiO_2$ quasi-binary system in clove oil : (*a*) Lamellar twinning in $15Na_2O.5P_2O_5.6SiO_2$ peritectic compound (× 400) ; (*b*) conglomerates of $2Na_2O.P_2O_5$ and $15Na_2O.5P_2O_5.6SiO_2$ (× 400) ; (*c*) the precipitation of white $15Na_2O.5P_2O_5.6SiO_2$ crystals on the iso-metric $9Na_2O.2P_2O_5.6SiO_2$ crystals (× 100) ; (*d*) large grain of $9Na_2O.2P_2O_5.6SiO_2$ glittered by the peritectic compound (× 400). All between crossed nicols.**

## Table II

### INVARIANT POINTS OF THE $Na_2O$–$P_2O_5$–$SiO_2$ TERNARY SYSTEM

| Type | Phases | Temp., °C. | $Na_2O$, mole-% | $P_2O_5$, mole-% | $SiO_2$, mole-% |
|---|---|---|---|---|---|
| | **(*a*) $Na_2O$–$SiO_2$ Binary System** | | | | |
| Peritectic | $2Na_2O.SiO_2 \rightleftharpoons Na_2O$ + liquid | 1118 | 58·53 | | 41·47 |
| Eutectic | $2Na_2O.SiO_2 + Na_2O.SiO_2$, liquid | 1022 | 56·12 | | 43·88 |
| Melting | $Na_2O.SiO_2$, liquid | 1088 | 50·00 | | 50·00 |
| Eutectic | $Na_2O.SiO_2 + Na_2O.2SiO_2$, liquid | 846 | 37·16 | | 62·84 |
| Melting | $Na_2O.2SiO_2$, liquid | 874 | 33·34 | | 66·66 |
| Eutectic | $Na_2O.2SiO_2$ + quartz, liquid | 793 | 25·50 | | 74·50 |
| Eutectic | $Na_2O.2SiO_2$ + tridymite, liquid | 782 | 24·80 | | 75·20 |
| Inversion | $\alpha$-$Na_2O.2SiO_2 \rightleftharpoons \beta$-$Na_2O.2SiO_2$ | 678 | ... | | ... |
| Unmixing | Solid solution of $Na_2O.2SiO_2$ with excess $Na_2O$ | 706 | ... | | ... |
| Unmixing | Solid solution of $Na_2O.2SiO_2$ with excess $SiO_2$ | 768 | ... | | ... |
| Inversion | Quartz, tridymite, liquid | 870 | 23·90 | | 76·10 |
| Inversion | Tridymite, cristobalite, liquid | 1470 | 11·00 | | 89·00 |
| Melting | Cristobalite, liquid | 1713 | 0·00 | | 100·00 |
| | **(*b*) $Na_2O$–$P_2O_5$ Binary System** | | | | |
| Melting | $\alpha$-$3Na_2O.P_2O_5$ + liquid | 1583 | 75·00 | 25·00 | |
| Inversion | $\alpha$-$3Na_2O.P_2O_5$, $\beta$-$3Na_2O.P_2O_5$, liquid | 1474 | 74·10 | 25·90 | |
| Eutectic | $\beta$-$3Na_2O.P_2O_5 + 2Na_2O.P_2O_5$, liquid | 944 | 69·75 | 30·25 | |
| Melting | $2Na_2O.P_2O_5$, liquid | 978 | 66·67 | 33·33 | |
| Eutectic | $2Na_2O.P_2O_5 + Na_2O.P_2O_5$, liquid | 546 | 57·00 | 43·00 | |
| Melting | $Na_2O.P_2O_5$, liquid | 588 | 50·00 | 50·00 | |
| | **(*c*) $3Na_2O.P_2O_5$–$Na_2O.SiO_2$ Quasi-Binary System** | | | | |
| Melting | $\alpha$-$3Na_2O.P_2O_5$, liquid | 1583 | 75·00 | 25·00 | 0·00 |
| Inversion | $\alpha$-$3Na_2O.P_2O_5$, $\beta$-$3Na_2O.P_2O_5$, liquid | 1474 | 71·87 | 21·85 | 6·28 |
| Eutectic | $\beta$-$3Na_2O.P_2O_5 + Na_2O.SiO_2$, liquid | 1020 | 58·08 | 7·80 | 34·12 |
| Melting | $Na_2O.SiO_2$, liquid | 1088 | 50·00 | 0·00 | 50·00 |
| | **(*d*) $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ Quasi-Binary System** | | | | |
| Melting | $\alpha$-$3Na_2O.P_2O_5$, liquid | 1583 | 75·00 | 25·00 | 0·00 |
| Inversion | $\alpha$-$3Na_2O.P_2O_5$, $\beta$-$3Na_2O.P_2O_5$, liquid | 1474 | 71·48 | 22·88 | 5·64 |
| Eutectic | $\beta$-$3Na_2O.P_2O_5 + 9Na_2O.2P_2O_5.6SiO_2$, liquid | 1044 | 55·30 | 13·25 | 31·45 |
| Melting | $9Na_2O.2P_2O_5.6SiO_2$, liquid | 1100 | 53·04 | 11·82 | 35·14 |
| Peritectic | $5Na_2O.P_2O_5.4SiO_2 \rightleftharpoons 9Na_2O.2P_2O_5.6SiO_2$, liquid | 953 | 39·74 | 3·85 | 56·41 |
| Eutectic | $5Na_2O.P_2O_5.4SiO_2 + Na_2O.2SiO_2$, liquid | 838 | 35·57 | 1·37 | 63·06 |
| Melting | $Na_2O.2SiO_2$, liquid | 874 | 33·33 | 0·00 | 66·67 |
| | **(*e*) $2Na_2O.P_2O_5$–$9Na_2O.2P_2O_5.6SiO_2$ Quasi-Binary System** | | | | |
| Melting | $2Na_2O.P_2O_5$, liquid | 978 | 66·67 | 33·33 | 0·00 |
| Eutectic | $2Na_2O.P_2O_5 + 15Na_2O.5P_2O_5.6SiO_2$, liquid | 912 | 62·92 | 26·92 | 10·16 |
| Peritectic | $15Na_2O.5P_2O_5.6SiO_2 \rightleftharpoons 9Na_2O.2P_2O_5.6SiO_2$ + liquid | 987 | 59·90 | 21·98 | 18·12 |
| Melting | $9Na_2O.2P_2O_5.6SiO_2$, liquid | 1100 | 53·04 | 11·82 | 35·14 |
| | **(*f*) $2Na_2O.P_2O_5$–$SiO_2$ Quasi-Binary System** | | | | |
| Melting | $2Na_2O.P_2O_5$, liquid | 978 | 66·67 | 33·33 | 0·00 |
| Eutectic | $2Na_2O.P_2O_5$ + tridymite, liquid | 961 | 54·41 | 27·20 | 18·39 |
| Inversion | Tridymite, cristobalite, liquid | 1470 | ... | ... | ... |
| Melting | Cristobalite, liquid | 1713 | ... | ... | 100·00 |
| | **(*g*) $3Na_2O.P_2O_5$–$Na_2O.SiO_2$–$Na_2O.2SiO_2$ Partial Ternary System** | | | | |
| Peritectic $Tp_1$ | $3Na_2O.P_2O_5 + Na_2O.SiO_2 \rightleftharpoons 9Na_2O.2P_2O_5.6SiO_2$ + liquid $Tp_1$ | 936 | 43·40 | 3·50 | 53·10 |
| Peritectic $Tp_2$ | $9Na_2O.2P_2O_5.6SiO_2 + Na_2O.SiO_2 = 5Na_2O.P_2O_5.4SiO_2$ + liquid $Tp_2$ | 920 | 41·60 | 2·70 | 55·70 |
| Eutectic $E_1$ | $5Na_2O.P_2O_5.4SiO_2 + Na_2O.SiO_2 + Na_2O.2SiO_2$, liquid $E_1$ | 816 | 36·80 | 1·00 | 62·20 |
| | **(*h*) $3Na_2O.P_2O_5$–$9Na_2O.2P_2O_5.6SiO_2$–$2Na_2O.P_2O_5$ Partial Ternary System** | | | | |
| Peritectic $Tp_3$ | $3Na_2O.P_2O_5 + 9Na_2O.2P_2O_5.6SiO_2 \rightleftharpoons 15Na_2O.5P_2O_5.6SiO_2$ + liquid $Tp_3$ | 950 | 59·50 | 21·50 | 19·00 |
| Eutectic $E_2$ | $3Na_2O.P_2O_5 + 15Na_2O.5P_2O_5.6SiO_2 + 2Na_2O.P_2O_5$, liquid | 900 | 62·70 | 26·80 | 10·50 |

Sodium di-silicate melts at 874° C. according to Morey and Bowen, and the same melting point has been recorded by the authors. The meta-silicate/di-silicate eutectic is located at 62·8 mole-% $SiO_2$ and 846° C. The di-silicate/quartz eutectic is at 74·5 mole-% $SiO_2$ and 793° C. The metastable eutectic between sodium di-silicate and tridymite is at 75·2 mole-% $SiO_2$ and 782° C.

The silica crystallizes from sodium silicate melts in three forms : cristobalite, tridymite, and quartz, the inversion temperatures being 1470° and 870° C. The cristobalite liquidus descends from its melting point, 1713° C., to the inversion point between cristobalite and tridymite, located at 89·0 mole-% $SiO_2$ and 1470° C. The inflexion in the curve shows a slight positive tendency towards an immiscibility gap. In the alkali-silicate melts, however, the silica-saturated liquid does not separate into two phases. The tridymite liquidus then descends smoothly from this point. At 76·10 mole-% $SiO_2$ and 870° C. it meets the liquidus curve of quartz. Morey and Bowen found that $Na_2O.2SiO_2$ takes up into solution both excess $Na_2O$ and $SiO_2$. It undergoes an allotropic change at 678° C.

The data so far obtained for the alkali silicate systems point to a progressive change of stability from the meta-silicates to di-silicates as the atomic weight of the alkali increases. It is now known that in the case of lithium and sodium the meta-silicate is unquestionably the most stable compound, but in the case of potassium and rubidium, it is the di-silicate.

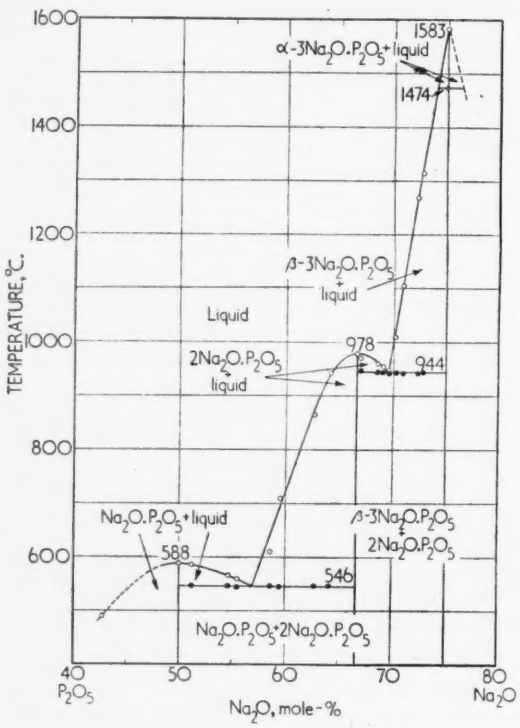



**Fig. 13—Phase-equilibrium diagram of the $Na_2O$–$P_2O_5$ binary system**

The microphotographs of sodium meta-silicate are shown in Fig. 6. Figure 6*a* is a slice of usual thickness, and between crossed nicols it shows well-defined cleavage. Its habit of crystallization is needle-like, as in Fig. 6*b*. It is biaxial, belonging to the orthorhombic crystal system. Its optic sign is negative, and the optic angle is large. There are two sets of cleavages ; one is parallel to the *c*-axis, giving a 0° extinction angle, and the other is at 20° with extinction. On crushing, it readily splits along one of the cleavage planes, and it is rarely possible to see two sets of cleavages on a fragment. The refractive indices using sodium light are : $N_m = 1{\cdot}520$, $\alpha = 1{\cdot}513$, $\beta = 1{\cdot}520$, and $\gamma = 1{\cdot}528$. The specific gravity is 2·546 g./c.c.

The interference colours are green, yellow, and pink of the second order, and the birefringence is about 0·015. The crushed crystals tend to form bevelled edges, so that they display interference colour bands, shown in Figs. 6*c* and *d*. Figure 6*c* also shows the inclined cleavage planes. This compound is also hygroscopic, and so the crystals appear to have slightly mottled surfaces (*see* Figs. 6*c* and *d*).

A micro-slice of sodium di-silicate is shown in Fig. 7*a*. Its acicular mode of formation gives it the appearance of a fibrous structure. Perfect cleavage is parallel to the *c*-axis, along which the crystal is elongated to form the needles. It is biaxial negative, and has an orthorhombic prism form with about 52° optic angle (*see* Figs. 7*b* and *c*). The refractive indices using sodium light are $N_m = 1{\cdot}502$, $\alpha = 1{\cdot}497$, $\beta = ?$, $\gamma = 1{\cdot}508$. The specific gravity is 2·484 g./c.c.

The interference colours are yellow, pink, and blue of the first order, and a green patch may sometimes be seen on the thick part of the fragment. The birefringence is not greater than 0·012. This compound is more hygroscopic than the meta-silicate, and under the microscope the surface of the crystals has a mottled appearance.

The optical properties of $SiO_2$ in its various forms are well known.

### Sodium Oxide–Phosphorus Pentoxide Binary System

The $Na_2O$–$P_2O_5$ binary system has apparently not been investigated. The three compounds, *i.e.*, tri-basic sodium phosphate or sodium ortho-phosphate ($3Na_2O.P_2O_5$), sodium pyro-phosphate ($2Na_2O.P_2O_5$), and sodium meta-phosphate ($Na_2O.P_2O_5$), are known.

Melts in this series were made with mixtures of these three compounds. The phase-equilibrium diagram of the $Na_2O$–$P_2O_5$ system is shown in Fig. 13. The range of composition within which the system has been investigated lies between $3Na_2O.P_2O_5$ and $Na_2O.P_2O_5$. The composition range investigated was limited because $Na_2O$ and $P_2O_5$ both possess high vapour pressures and consequently sublime at temperatures far below their melting points. There are also other difficulties connected with the handling of the melts that contain free $Na_2O$.

According to the present experiments, $3Na_2O.P_2O_5$ has a congruent melting point at 1583° C., and undergoes an allotropic phase change at 1474° C. An increase in the percentage of $P_2O_5$ lowers the melting

point of the ortho-phosphate along the liquidus curve, which ends at the $3Na_2O.P_2O_5/2Na_2O.P_2O_5$ eutectic, *i.e.*, 69·8 mole-% $Na_2O$ at 944° C. However, an increase in the $P_2O_5$ content of the melt by about 5 mole-% lowers the melting point of the ortho-phosphate by 640° C. As the percentage of $P_2O_5$ increases beyond the eutectic composition, the liquidus curve rises, and its slope decreases considerably as the composition of the melt approaches that of the pyro-phosphate.

Sodium pyro-phosphate melts at 978° C.; on cooling it crystallizes very readily, even with rapid rates of cooling. The liquidus curve of the pyro-phosphate on the $P_2O_5$ side of the compound ends at the $2Na_2O.P_2O_5/Na_2O.P_2O_5$ eutectic, *i.e.*, 57·0 mole-% $Na_2O$ at 546° C.

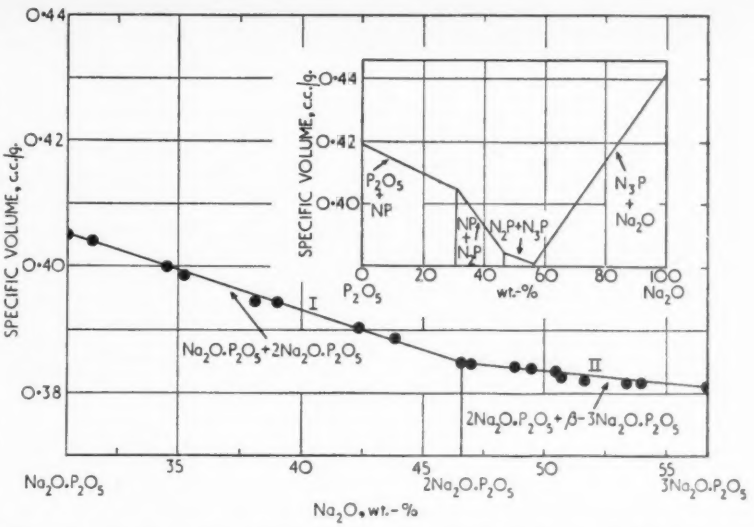



**Fig. 14—Specific volume/composition relationship of the $Na_2O$–$P_2O_5$ binary system**

No difficulty was found in obtaining reproducible data on the melts whose compositions lay between 57·0 and 75·0 mole-% $Na_2O$. With melts of higher $P_2O_5$ contents, the rate of cooling had to be reduced to about 0·15° C./min., but even then it was impossible to crystallize the primary phase, *i.e.*, meta-phosphate, with continuous cooling. The heating curve was obtained as explained before. By this means, reliable arrests corresponding to the solidus and liquidus of the mixture were obtained. Figure 13 shows that the eutectic temperatures on the meta-phosphate side of the $Na_2O.P_2O_5/2Na_2O.P_2O_5$ eutectic, which were obtained by heating, are identical with those on the pyro-phosphate side of the eutectic, which were obtained by cooling. By this method, *i.e.*, crystallizing and then heating to its melting point, it is found that $Na_2O.P_2O_5$ melts at 588° C. Only one melt, whose composition lies on the $P_2O_5$ side of the meta-phosphate, was analysed; this mixture melts at 490° C., which may be considered to lie on the meta-phosphate liquidus, as shown by the dotted curve in Fig. 13.

The liquidus curves near the compounds become flatter as their $P_2O_5$ contents increase, and it may be suggested that the degree of stability of the phosphate increases as its composition approaches that of the ortho-phosphate.

In Fig. 14 the specific volume is plotted against the wt.-% of $Na_2O$; since the specific volume is represented in c.c./g., the composition has been expressed in terms of weight percentages. The limit of the investigation in the $Na_2O$–$P_2O_5$ binary system lies between the three compounds of sodium phosphate, and within this range of composition there appear to be two straight lines whose intersection lies on the middle compound, pyro-phosphate. The lines I and II are related to the conglomerates of sodium meta-phosphate/pyro-phosphate and pyro-phosphate/ortho-phosphate respectively. The specific volumes of $Na_2O$ and $P_2O_5$ are known to be 0·4405 and 0·4189 c.c./g. respectively. On this basis the entire system may take the form drawn in the inset diagram in Fig. 14.

An endeavour was made to show the existence of high- and low-temperature phases in the ortho-phosphate. The β-$3Na_2O.P_2O_5$ could easily be obtained by slow cooling. This phase change is indicated by the arrest on the cooling curve of Fig. 4. On heating, however, this phase change appears to be rather sluggish. The high-temperature phase, *i.e.*, α-$3Na_2O.P_2O_5$, could be partly retained by quenching from 1500° C. The densities of the (α + β) and the β phases are 2·662 and 2·625 g./c.c. respectively.

The structure of a micro-slice of the high-temperature phase observed through crossed nicols is shown in Figs. 8*a* and *b*. There appear to be three sets of parallel planes (white in the microphotograph) that throughout one grain extinguish at the same angle, the background remaining extinct for 360°. This leads to the conclusion that there are two phases. The matrix is isotropic and the crystals along parallel planes are anisotropic. It is evident that the isotropic crystals of α-$3Na_2O.P_2O_5$ are partly retained on quenching. The rate of quenching was apparently not rapid enough to retain the α-$3Na_2O.P_2O_5$ phase, and allowed the β-phase to precipitate along its (111) planes. In addition, the extinction of the α-phase is parallel to one of the sets of planes along which the grain under ordinary light appears to be striated (along N–E direction in Fig. 8*b*).

The β-$3Na_2O.P_2O_5$ crystals obtained by slow cooling through the inversion temperature 1474° C. are rather small, and little information can be obtained about their optical properties. The grains are irregular in shape, more often with rounded corners, and there is no distinct cleavage. All sections show lamellar twinning in two directions (*see* Fig. 9). The mean refractive index $N_m$ is 1·535. It gives low interference colours, being dark-grey to white of the first order.

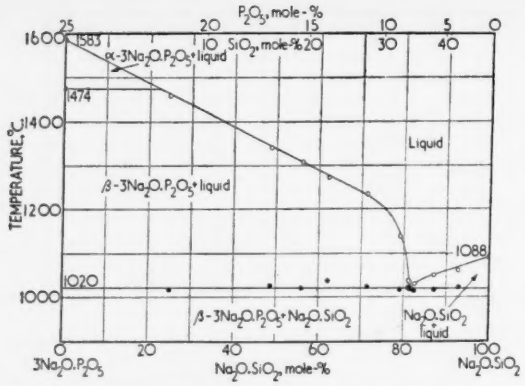



**Fig. 15—Phase-equilibrium diagram of the $3Na_2O.P_2O_5$–$Na_2O.SiO_2$ quasi-binary system**

The birefringence is about 0·004 to 0·005. It is believed to be uniaxial, but the interference figures, in convergent light between crossed nicols, are very poor. The lamellar twinning, which is the diagnostic feature of this phase, is identical with that of calcite, whose crystal system is hexagonal and in which this type of twinning is quite common. It is, therefore, safe to assume that the β-$3Na_2O.P_2O_5$ belongs to a hexagonal crystal system, with its *c*-axis similar to its *a*-axes.

The $2Na_2O.P_2O_5$ forms well-developed crystals on a moderate rate of cooling. Its mode of crystallization is plate-like. It has a perfect cleavage plane parallel to the *c*-axis. A basal section in Fig. 10*a* shows the well-defined cleavage planes. In all sections inclined to the base the extinction is parallel to the cleavage planes. The vertical and the basal sections give perfect interference figures under convergent light. It is uniaxial positive. Most of the sections are four-sided, giving straight extinctions. It therefore becomes evident that the pyro-phosphate belongs to the tetragonal crystal system.

The mean refractive index of $2Na_2O.P_2O_5$ is 1·525, and the sections along a cleavage plane give the highest interference colours, which are green, yellow, and pinkish-red of the first order. The birefringence is about 0·025. There is no sign of alteration, and the sections appear very clearly under the microscope. There is no twinning.

The crystals of $Na_2O.P_2O_5$ are well developed, and they show two sets of cleavages. The rhombic cleavages are faintly revealed on the section which is taken along the other cleavage, *i.e.*, parallel to the vertical axis (Fig. 11*a*). On this section, the extinction is at 30° with the rhombic cleavage. The section along the rhombic cleavage in Fig. 11*b* shows cleavage planes which give straight extinction. The vertical and the basal sections show good interference figures. It is uniaxial negative.

The mean refractive index of $Na_2O.P_2O_5$ is 1·500. It gives high polarization colours, being between the second and third order of Newton's scale. The birefringence is about 0·028.

The major part of the basal section of the meta-phosphate is shown in Fig. 11*c*. It evidently belongs to the hexagonal crystal system, crystallizing in a prismatic form.

The $Na_2O.P_2O_5$ is rather hygroscopic, and consequently the crystals appear mottled. The crystals appear slightly grey to light-brown under ordinary light, which may be due to the absorption of the light. Twinning is not present.

### Phosphorus Pentoxide–Silica Binary System

In the study of the phase relations in the CaO–$P_2O_5$–$SiO_2$ ternary system[4] it was pointed out that there was an immiscibility gap in the liquid phase in the regions high in $P_2O_5$ and $SiO_2$. One of the compositions that gave two liquids at 1400° C. was 23% CaO, 20% $SiO_2$, and 57% $P_2O_5$. It is therefore expected that the immiscibility gap in the $P_2O_5$–$SiO_2$ binary system may extend into the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system to form a semi-dome.

## QUASI-BINARY SECTIONS

There are three stable compounds in the $Na_2O$–$P_2O_5$ binary system, and one peritectic and two stable compounds in the $Na_2O$–$SiO_2$ binary system. The components of the partial ternary systems must be stable at their melting points, and each pair must form a quasi-binary system. In the present research four such sections have been studied.

### $3Na_2O.P_2O_5$–$Na_2O.SiO_2$ System

Twelve melts were made; the phase-equilibrium diagram is shown in Fig. 15, where the composition is given in terms of molecular percentages of sodium meta-silicate. The invariant points of the system are given in Table II*c*.

The section appears to be of a eutectiferous type. At 1474° C. the invariant horizontal line of $3Na_2O.P_2O_5$ cuts the liquidus curve at 22·3 mole-% $Na_2O.SiO_2$. As the molecular percentage of $Na_2O.SiO_2$ increases from 0–71·5, the melting point of the slag falls from 1583° to 1235° C., and the liquidus curve within these limits is a straight line. It was within this area that no difficulty was experienced in the crystallization of the slags. The slope of the phosphate liquidus curve increases very rapidly as the percentage of the meta-silicate increases, and there appears to be a eutectic at 81·4 mole-% $Na_2O.SiO_2$ and 1020° C. Within the field where $Na_2O.SiO_2$ is the primary crystal, the average rate of cooling should not exceed 0·3° C./min. if the slag is required to be crystalline. The authors are not prepared to make any suggestion as to the extent of the partial solubility which may exhibit itself in the extreme ends of the system, because the present experimental methods cannot be regarded as adequate enough for the purpose. There is, however, little or no change in the position of the lines in the X-ray powder patterns, which indicates the absence of solid solubility, a view that is substantiated by specific volume determinations.

It is evident from Fig. 16, where the specific volumes of the slags are plotted against the weight percentages of $Na_2O.SiO_2$, that the straight line drawn through the experimental points suggests that $3Na_2O.P_2O_5$ and $Na_2O.SiO_2$ form a simple eutectiferous binary system.

These two phases are easily recognized under the petrological microscope by their distinct optical properties.

### $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ System

This is the most complicated system that has been investigated. The phase-equilibrium diagram of this system is drawn in Fig. 17, where the composition is given in molecular percentages of sodium di-silicate.

The experimental evidence points to the fact that in this system there is one stable and one peritectic compound; these are in fact two ternary compounds with congruent and incongruent melting points respectively. According to the phase diagram in Fig. 17, the composition of the stable compound is 60·0 mole-% $Na_2O.2SiO_2$ and 40·0 mole-% $3Na_2O.P_2O_5$, that is, 53·04 mole-% $Na_2O$, 11·82 mole-% $P_2O_5$, and 35·14 mole-% $SiO_2$. It has a congruent melting point at 1100° C. It is clear that in this compound the ratio $3Na_2O.P_2O_5$ : $Na_2O.2SiO_2$ is 2 : 3. In other words, the compound in question consists of two molecules of $3Na_2O.P_2O_5$ and three molecules of $Na_2O.2SiO_2$. Therefore, the formula of this compound may be written as $2(3Na_2O.P_2O_5).3(Na_2O.2SiO_2)$, that is, $9Na_2O.2P_2O_5.6SiO_2$. The sharpness of the liquidus curve in the vicinity of the compound suggests that $9Na_2O.2P_2O_5.6SiO_2$ is quite stable above its melting point. Between ortho-phosphate and the ternary compound, there appears to be a eutectic at 31·45 mole-% $SiO_2$ and 1044° C. The liquidus curve of the ortho-phosphate is a straight line, and the inversion point of ($\alpha$-$3Na_2O.P_2O_5$)/($\beta$-$3Na_2O.P_2O_5$ and liquid) is at 5·64 mole-% $SiO_2$ and 1474° C. (*see* Table II*d*).

As the molecular percentage of $Na_2O.2SiO_2$ increases from 60 to 90, the liquidus curve of the compound $9Na_2O.2P_2O_5.6SiO_2$ gradually slopes down, as shown in Fig. 17. Within this range of composition, the primary crystals of $9Na_2O.2P_2O_5.6SiO_2$ react with liquid (56·4 mole-% $SiO_2$) at 953° C. The result of this reaction is the formation of a peritectic compound that evidently consists of one molecule of $3Na_2O.P_2O_5$ and two molecules of $Na_2O.2SiO_2$. This may be written as $(3Na_2O.P_2O_5).2(Na_2O.2SiO_2)$, that is, $5Na_2O.P_2O_5.4SiO_2$. The composition of this compound is 66·67 mole-% $Na_2O.2SiO_2$, and 33·33 mole-% $3Na_2O.P_2O_5$, that is, 50·0 mole-% $Na_2O$, 10·0 mole-% $P_2O_5$, and 40·0 mole-% $SiO_2$.

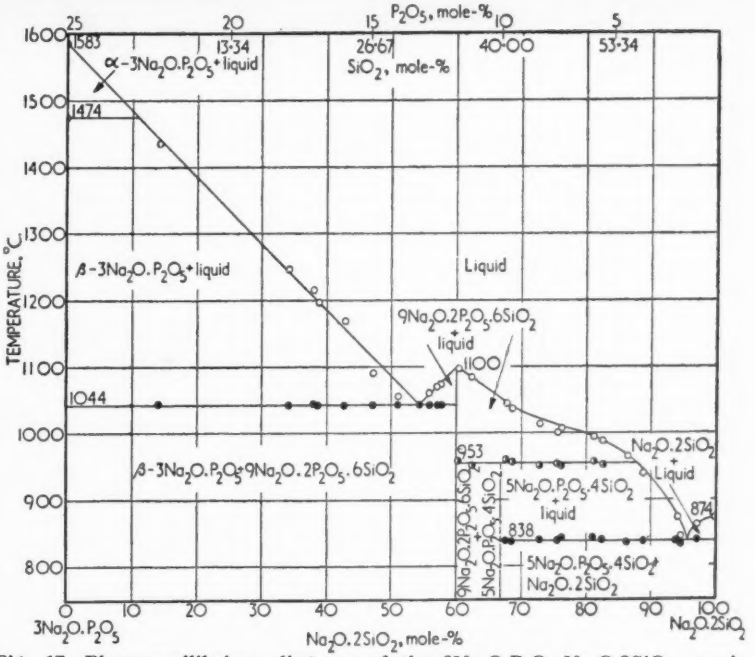



**Fig. 17—Phase-equilibrium diagram of the $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ quasi-binary system**

When the melts containing 88–95 mole-% $Na_2O.2SiO_2$ are cooled below 953° C., the primary crystals are of $5Na_2O.P_2O_5.4SiO_2$. Finally, there is a eutectic between the peritectic compound and $Na_2O.2SiO_2$ at 63·1 mole-% $SiO_2$ and 838° C. Beyond the composition of the eutectic, the liquidus curve rises to 874° C., the melting point of $Na_2O.2SiO_2$. It may be observed that the primary crystallization range of $Na_2O.2SiO_2$ is rather small.

There are four crystalline phases in this system, which is thus divided into three sections, in each of which two of the phases coexist. This is evidenced by the specific volumes of the slags, whose compositions lie on the $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ section. In Fig. 18 the specific volume is plotted against the weight percentage of $Na_2O.2SiO_2$. The scatter of the experimental points is greater than usual, if compared with the other diagrams. This may be attributed to a slight deviation of the slag composition from the $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ section. Nevertheless, it is clear that the experimental points are located fairly closely about the three lines drawn in Fig. 18. It is, however, interesting to note that the compositions at which the lines change direction correspond with those of the compounds shown in Fig. 17.

In spite of the faintness of the lines in the X-ray powder patterns, the existence of the above-mentioned compounds is substantiated.

Microscopic examination of the slags lying in this section was informative, although little information

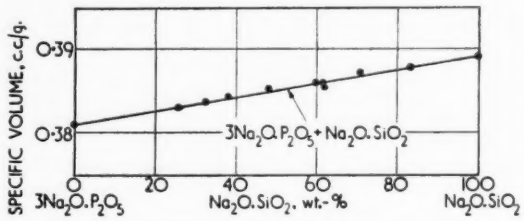



**Fig. 16—Specific volume/composition relationship of the $3Na_2O.P_2O_5$–$Na_2O.SiO_2$ quasi-binary system**

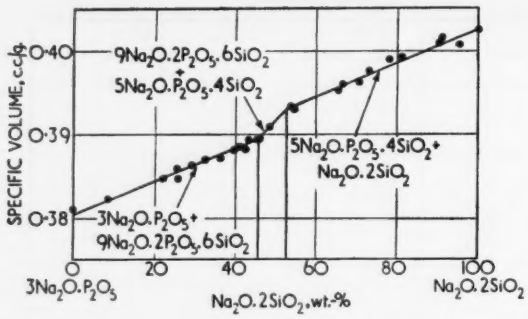



**Fig. 18—Specific volume/composition relationship of the $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ quasi-binary system**

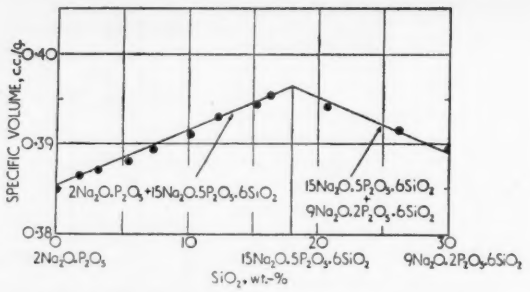



**Fig. 20—Specific volume/composition relationship of the $2Na_2O.P_2O_5$–$9Na_2O.2P_2O_5.6SiO_2$ quasi-binary system**

was obtained about the optical properties of these two compounds. The refractive index of the ternary stable compound is 1·520, and that of the peritectic compound is 1·515. The former is isotropic and the latter anisotropic.

### $2Na_2O.P_2O_5$–$9Na_2O.P_2O_5.6SiO_2$ System

The phase-equilibrium diagram of the $2Na_2O.P_2O_5$–$9Na_2O.2P_2O_5.6SiO_2$ quasi-binary system is drawn in Fig. 19. The crystallization of the melts was most satisfactory.

It may be observed that as the percentage of the pyro-phosphate increases, the melting point of the ternary compound decreases very little at first, but eventually the slope of the liquidus rises very materially. It is also interesting to note that although melts (2*E*)2 and (2*E*)3 showed two arrests on cooling and were solid just below 987° C., melts (2*E*)4 and (2*E*)5 gave three arrests on cooling and were not solid before 912° C. was reached. Consequently, it was expected that there should be a peritectic compound whose composition lies between the composition of melts (2*E*)3 and (2*E*)4. Furthermore, the composition

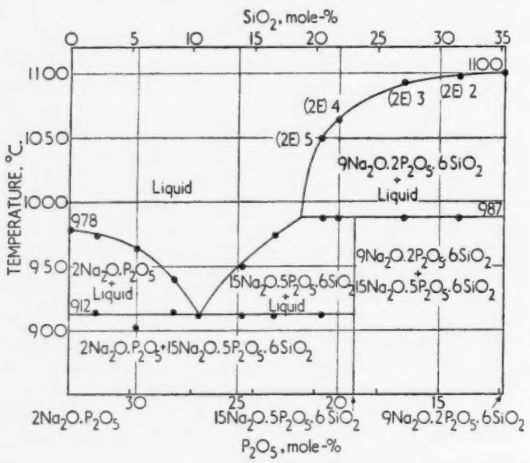



**Fig. 19—Phase-equilibrium diagram of the $2Na_2O.P_2O_5$–$9Na_2O.2P_2O_5$–$6SiO_2$ quasi-binary system**

of this compound must be such that its formula can be represented by whole numbers. The only compound that might satisfy these conditions is $15Na_2O.5P_2O_5.6SiO_2$. This compound apparently melts at 987° C., and at the same time dissociates into its reactants, thus:

$$15Na_2O.5P_2O_5.6SiO_2 \rightleftharpoons 9Na_2O.2P_2O_5.6SiO_2 + \text{melt} \quad \ldots(1)$$

The composition of the peritectic compound is 25·0 mole-% $9Na_2O.2P_2O_5.6SiO_2$, and 75·0 mole-% $2Na_2O.P_2O_5$, that is, 57·7 mole-% $Na_2O$, 19·23 mole-% $P_2O_5$, and 23·07 mole-% $SiO_2$. This compound also lies on the $3Na_2O.P_2O_5$–$SiO_2$ section.

When the composition of the melt travels towards the $2Na_2O.P_2O_5$, the liquidus curve of the $15Na_2O.5P_2O_5.6SiO_2$ phase slopes further below the peritectic temperature and ends on the eutectic at 26·9 mole-% $P_2O_5$ and 912° C. Any further increase in the $P_2O_5$ content of the melt raises the liquidus temperature, and the slope of the pyro-phosphate liquidus curve decreases as the composition of the melt becomes nearer to that of $2Na_2O.P_2O_5$.

Support for the above results may be obtained by considering the variation of specific volume with composition along this section. The location of the experimental points in Fig. 20 indicates two specific-volume lines whose intersection point has the composition corresponding to that of the peritectic compound, with a maximum specific volume. The X-ray powder patterns of the slags on this section are quite compatible with these findings.

Between crossed nicols the compound $15Na_2O.5P_2O_5.6SiO_2$ shows well-defined twins, as shown in Figs. 12*a* and *b*. The lamellar twinning is easily recognized in these anisotropic crystals. In Fig. 12*b* a few $2Na_2O.P_2O_5$ flakes are distinguishable by their polarization colour rings and the absence of twinning. The mean refractive index of the peritectic compound is 1·510. As the composition of the slag travels further towards the ternary stable compound $9Na_2O.2P_2O_5.6SiO_2$, the $2Na_2O.P_2O_5$ disappears completely, and is replaced by the ternary stable compound, which is isometric. The peritectic compound that precipitates on these isometric crystals is seen as white dots or fine lines in Figs. 12*c* and *d*. The precipitation of the other peritectic compound $5Na_2O.P_2O_5.4SiO_2$ gives an appearance similar to that of the isotropic stable compound.

### $2Na_2O.P_2O_5$–$SiO_2$ System

The phase-equilibrium diagram of this system is drawn in Fig. 21. The composition along the bottom abscissa is in molecular percentages of $SiO_2$, so that $2Na_2O.P_2O_5$ mole-% + $SiO_2$ mole-% = 100. The top abscissa, however, gives the molecular percentages of $SiO_2$ and $P_2O_5$, so that $Na_2O$ mole-% + $P_2O_5$ mole-% + $SiO_2$ mole-% = 100. This is a simple eutectic system, and the melts can readily be crystallized at a moderate rate of cooling, *e.g.*, 1·0° C./min. The solidification range of $2Na_2O.P_2O_5$ appears to be very narrow, being about 17° C. in the vicinity of the pyrophosphate.

The eutectic of the system lies at 59·7 mole-% $2Na_2O.P_2O_5$ and 961° C. (*see* Table II*f*). Any further increase in the $SiO_2$ content of the melt raises the melting point of the slag at a rapid rate ; as may be observed, the experimental points lie on a straight line, which is the liquidus curve of the tridymite primary phase. The eutectic temperature for each melt on this side of the system is again very consistent. Unfortunately, the present experimental conditions did not allow the authors to extend the investigation of the system towards the higher $SiO_2$ regions, because, with the high-temperature furnace used, no melts could be made at temperatures higher than 1600° C. The slope of the liquidus suggests that the mixture containing about 70 mole-% $SiO_2$ and 30 mole-% $2Na_2O.P_2O_5$ will not melt below 1600° C. The authors are aware that there is an extensive immiscibility gap in the $P_2O_5$/$SiO_2$-rich melts, and it is expected that this immiscibility gap may extend into the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system to form a semi-dome. The primary phase in this part of the system is most probably cristobalite, which should be transformed to tridymite at 1470° C. Since the eutectic temperature is 961° C., the slag below this temperature will consist of conglomerates of $2Na_2O.P_2O_5$ and tridymite.

Incidentally, after the attainment of the solidus temperature, the slag was water quenched in all the melts so that the crystalline slag was not subject to any phase transformation below its eutectic temperature. The efficiency of quenching to retain the phases just below its eutectic may be shown by the following illustration.

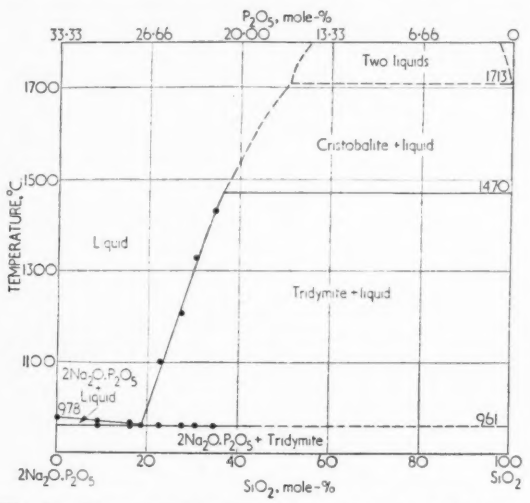



**Fig. 21—Phase-equilibrium diagram of the $2Na_2O.P_2O_5$–$SiO_2$ quasi-binary system**

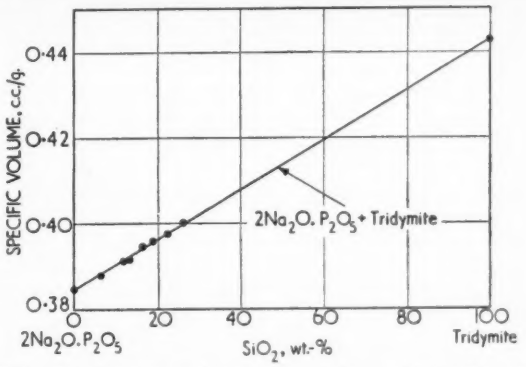



**Fig. 22—Specific volume composition relationship of the $2Na_2O.P_2O_5$–$SiO_2$ quasi-binary system**

It is evident from Fig. 22 that the components of this system form a eutectiferous mixture. Although the figure is lacking in experimental points in the regions which contain greater than 30 mole-% $SiO_2$, all the experimental points lie on a straight line joining the specific volume of pyro-phosphate to that of tridymite. The specific volume of tridymite is 0·4425 and that of quartz is 0·3773, and there is no doubt about the absence of quartz in the slags of this system.

## PARTIAL TERNARY SYSTEMS

### $3Na_2O.P_2O_5$–$Na_2O.SiO_2$–$Na_2O.2SiO_2$ System

Since two sides of this triangle are quasi-binary systems and the third is a binary, the area within these sides may be treated as a partial ternary system. The liquidus surfaces of the system are shown in Fig. 23, where the composition is given in molecular percentages of the initial components $Na_2O$, $P_2O_5$, and $SiO_2$. The position of the partial ternary in relation to the complete ternary is shown in the inset diagram in Fig. 23.

A few melts were sufficient to show that the $Na_2O.SiO_2$–$9Na_2O.2P_2O_5.6SiO_2$ section was not a quasi-binary system, and, furthermore, it became evident that the $3Na_2O.P_2O_5$ liquidus surface was overlapping the section between meta-silicate and the ternary compound.

The melting points of the eutectics $e^I$ and $e^{II}$ decrease as the percentage of the third component increases, and this is indicated by the positions of the isothermals. The melts whose composition falls on the curve $e^I Tp_1$ are saturated in $3Na_2O.P_2O_5$ and $Na_2O.SiO_2$. Furthermore, the melts that lie on the $e^{II}Tp_1$ are saturated in $3Na_2O.P_2O_5$ and $9Na_2O.2P_2O_5.6SiO_2$. Hence at $Tp_1$ there must be an invariant equilibrium. As the point $Tp_1$ is not within the triangle formed by the three solid phases $3Na_2O.P_2O_5$, $Na_2O.SiO_2$, and $9Na_2O.2P_2O_5.6SiO_2$, the present arrangement cannot correspond to a eutectic reaction, but is one of the type

$$3Na_2O.P_2O_5 + \text{melt } Tp_1 \rightleftharpoons 9Na_2O.2P_2O_5.6SiO_2 + Na_2O.SiO_2 \quad \ldots(2)$$

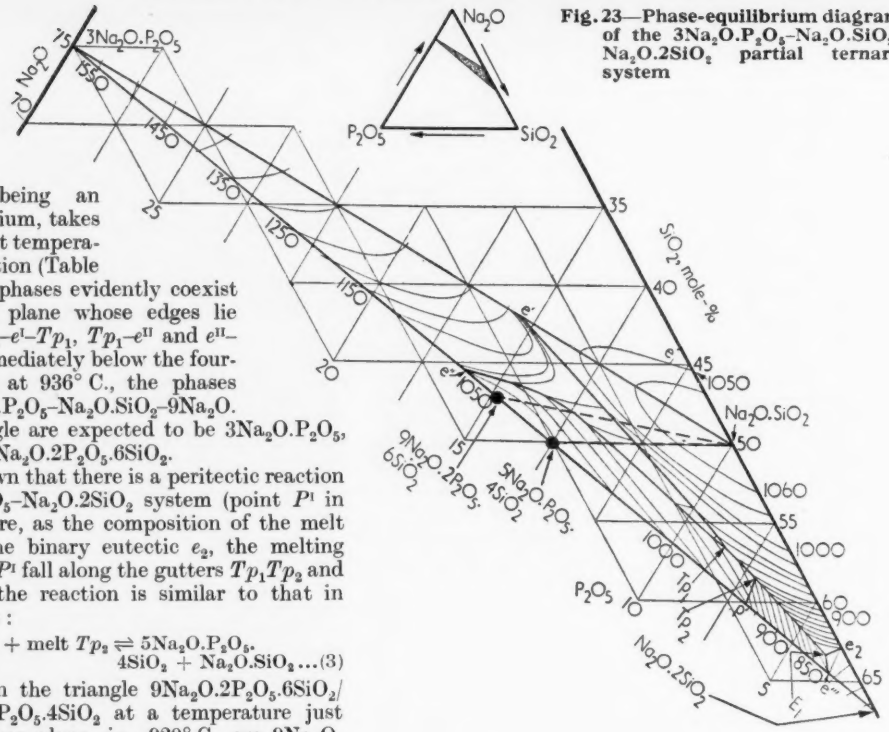



**Fig. 23—Phase-equilibrium diagram of the $3Na_2O.P_2O_5$–$Na_2O.SiO_2$–$Na_2O.2SiO_2$ partial ternary system**

The reaction, being an invariant equilibrium, takes place at a constant temperature and composition (Table II*g*). These four phases evidently coexist on a four-phase plane whose edges lie along $3Na_2O.P_2O_5$–$e^I$–$Tp_1$, $Tp_1$–$e^{II}$ and $e^{II}$–$3Na_2O.P_2O_5$. Immediately below the four-phase plane, *i.e.*, at 936° C., the phases within the $3Na_2O.P_2O_5$–$Na_2O.SiO_2$–$9Na_2O.2P_2O_5.6SiO_2$ triangle are expected to be $3Na_2O.P_2O_5$, $Na_2O.SiO_2$, and $9Na_2O.2P_2O_5.6SiO_2$.

It has been shown that there is a peritectic reaction in the $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ system (point $P^I$ in Fig. 23). Therefore, as the composition of the melt moves towards the binary eutectic $e_2$, the melting points of $Tp_1$ and $P^I$ fall along the gutters $Tp_1Tp_2$ and $P^ITp_2$. At $Tp_2$ the reaction is similar to that in equation (2), thus :

$$9Na_2O.2P_2O_5.6SiO_2 + \text{melt } Tp_2 \rightleftharpoons 5Na_2O.P_2O_5.4SiO_2 + Na_2O.SiO_2 \quad \ldots(3)$$

The phases within the triangle $9Na_2O.2P_2O_5.6SiO_2$/$Na_2O.SiO_2$/$5Na_2O.P_2O_5.4SiO_2$ at a temperature just below the four-phase plane, *i.e.*, 920° C., are $9Na_2O.2P_2O_5.6SiO_2$, $5Na_2O.P_2O_5.4SiO_2$, and $Na_2O.SiO_2$.

On cooling the liquid $Tp_2$, its composition travels along the gutter $Tp_2E_1$ where the liquid is saturated with $5Na_2O.P_2O_5.4SiO_2$, and $Na_2O.SO_2$. As the percentage of the third component increases, the eutectics $e_2$ and $e^{III}$ follow the gutters $e_2E_1$ and $e^{III}E_1$ respectively. Therefore, at point $E_1$ the liquid is saturated in three crystalline phases, which precipitate simultaneously at a constant temperature (816° C.). This arrangement corresponds to a eutectic reaction, because the point $E_1$ lies within the triangle formed by the three solid phases :

$$\text{liquid} \rightleftharpoons 5Na_2O.P_2O_5.4SiO_2 + Na_2O.SiO_2 + Na_2O.2SiO_2 \quad \ldots(4)$$

The ternary eutectic plane passes through three points occupied by the three crystalline phases stated in equation (4), and within this area the solid slag (just below the ternary eutectic temperature 816° C.) consists of the conglomerates of these three phases.

The compositions and the temperatures of the invariant points, *i.e.*, $Tp_1$, $Tp_2$, and $E_1$, are given in Table II*g*.

### $3Na_2O.P_2O_5$–$2Na_2O.P_2O_5$–$9Na_2O.2P_2O_5.6SiO_2$ System

The system is drawn in Fig. 24, where the composition is given in molecular percentages of $Na_2O$, $P_2O_5$, and $SiO_2$, and the area under investigation is shown

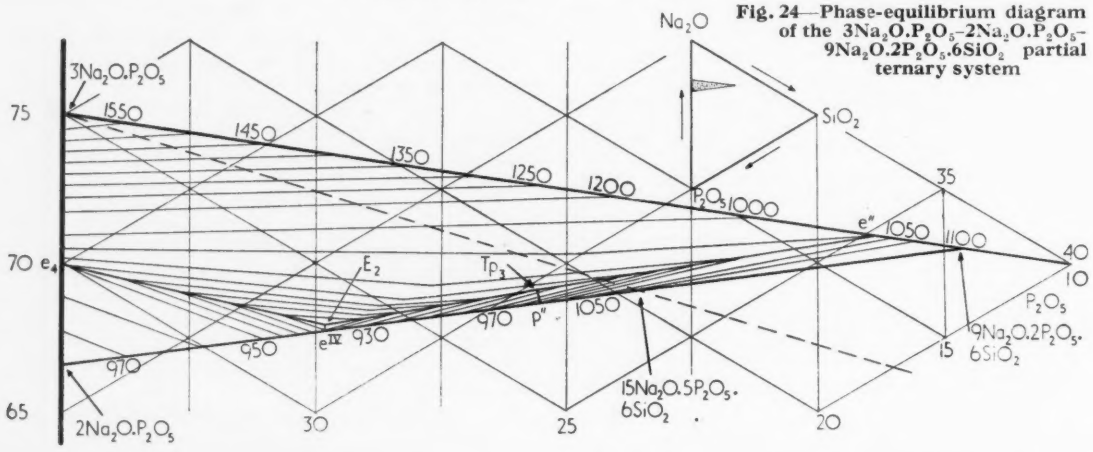



**Fig. 24—Phase-equilibrium diagram of the $3Na_2O.P_2O_5$–$2Na_2O.P_2O_5$–$9Na_2O.2P_2O_5.6SiO_2$ partial ternary system**

as an inset $Na_2O$–$P_2O_5$–$SiO_2$ triangle. The $3Na_2O.P_2O_5$ occupies a major part of the system, and the primary crystallization of the ternary compounds appears to have narrow ranges of composition. The construction of the system is similar to the $3Na_2O.P_2O_5$–$Na_2O.SiO_2$–$Na_2O.2SiO_2$ system. The eutectic and the peritectic points $e^{II}$ and $P^{II}$ travel along the gutters $e^{II}Tp_3$ and $P^{II}Tp_3$ respectively. The intersection point $Tp_3$ is the ternary peritectic point at 950° C. Within the triangle of $3Na_2O.P_2O_5$ and two ternary compounds, and below 950° C., the slags consist of $3Na_2O.P_2O_5$, $9Na_2O.2P_2O_5.6SiO_2$, and $15Na_2O.5P_2O_5.6SiO_2$.

The composition of the remainder of the liquid from the peritectic reaction

$$9Na_2O.2P_2O_5.6SiO_2 + \text{melt } Tp_3 \rightleftharpoons 15Na_2O.5P_2O_5.6SiO_2 + 3Na_2O.P_2O_5 \quad \ldots(5)$$

on further cooling travels along the gutter $Tp_3E_2$, and the eutectics $e_4$ and $e^{IV}$ follow the boundaries $e_4E_2$ and $e^{IV}E_2$. Therefore, $E_2$ is a ternary eutectic point (900° C.), and below this temperature the slags within this triangle contain crystals of $3Na_2O.P_2O_5$, $2Na_2O.P_2O_5$, and $15Na_2O.5P_2O_5.6SiO_2$. The invariant points are given in Table II*h*. The isothermals are shown quite clearly, and the rest of the diagram in Fig. 24 is self-explanatory.

## CONCLUSIONS

In that part of the system $Na_2O$–$P_2O_5$–$SiO_2$ which has been studied, there appear to be one stable and two peritectic compounds, which in the light of the experimental data are formulated as follows:

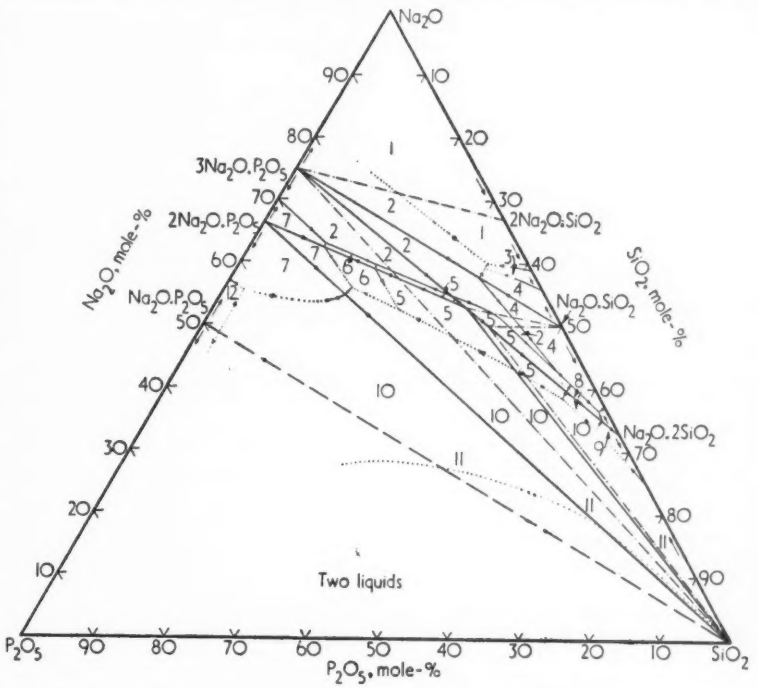
| | |
|---|---|
| Stable | $9Na_2O.2P_2O_5.6SiO_2$ m.p. 1100° C. |
| Unstable | $5Na_2O.P_2O_5.4SiO_2$ m.p. 953° C. |
| Unstable | $15Na_2O.5P_2O_5.6SiO_2$ m.p. 987° C. |

Between these and the other binary stable compounds there are eutectics. The present investigation indicates that the diagram takes the form shown in Fig. 25. That part of the diagram which has been determined is shown with full lines and the probable extension of this part is shown with broken lines. The liquidus surfaces are numbered, and the corresponding primary phases are included in Fig. 25.

The solidification of $Na_2O$ is presumed to commence on the primary liquidus surface (1). In this area there appears to be a peritectic reaction resulting in the formation of sodium ortho-silicate. The peritectic reaction is then followed by the ternary eutectic which consists of crystals of $3Na_2O.P_2O_5$, $2Na_2O.SiO_2$, and $Na_2O.SiO_2$. The area framed by $3Na_2O.P_2O_5$, $Na_2O.SiO_2$, and $Na_2O$ is believed to have little significance in the study of soda-slags and, keeping in mind the experimental difficulties already mentioned, no attempt has been made to investigate this part of the diagram.

The primary crystals of $3Na_2O.P_2O_5$ precipitate on the liquidus (2), which penetrates far into the system, and at $Tp_1$ (*see* Fig. 23) it reacts with liquid to form the $9Na_2O.2P_2O_5.6SiO_2$ ternary compound. Although this compound has a congruent melting point and a large liquidus surface (5), in slags containing increasing amounts of $Na_2O$, *i.e.*, above the $3Na_2O.P_2O_5$–$Na_2O.2SiO_2$ section, it decomposes into $3Na_2O.P_2O_5$ and liquid. This reaction may be attributed to the comparatively greater stability of the ortho-phosphate. The liquidus surfaces (6) and (8) of the other two peritectic compounds occupy rather small areas. The area of solidification producing $Na_2O.2SiO_2$ as a primary phase is also small.

The only sections that have not been studied lie between the $Na_2O.P_2O_5$–$SiO_2$ and $9Na_2O.2P_2O_5.6SiO_2$–$SiO_2$ sections. These sections will probably be eutectiferous, and they have been assumed to be so to construct the diagram. The tridymite liquidus surfaces may be represented by the surface (10). Knowing the section between $2Na_2O.P_2O_5$ and $SiO_2$, it is understandable that the primary crystallization of $SiO_2$ as




1: $Na_2O$
2: $3Na_2O.P_2O_5$
3: $2Na_2O.SiO_2$
4: $Na_2O.SiO_2$
5: $9Na_2O.2P_2O_5.6SiO_2$
6: $15Na_2O.5P_2O_5.6SiO_2$
7: $2Na_2O.P_2O_5$
8: $5Na_2O.P_2O_5.4SiO_2$
9: $Na_2O.2SiO_2$
10: Tridymite
11: Cristobalite
12: $Na_2O.P_2O_5$
13: $P_2O_5$

**Fig. 25—Phase-equilibrium diagram of the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system**

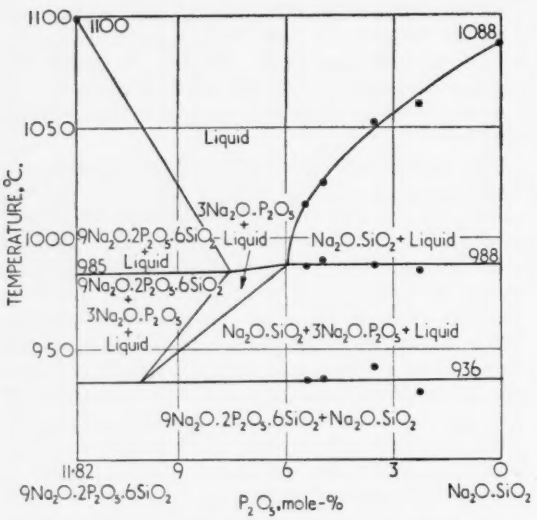



**Fig. 26—Phase-equilibrium diagram of the $NaO_2.SiO_2$–$9Na_2O.2P_2O_5.6SiO_2$ section**

tridymite, cristobalite and possibly quartz occupies such an extensive area in the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system.

The immiscibility boundary is denoted by the dotted curve. In the vicinity of this gap cristobalite is believed to be the primary phase. The difficulty in handling melts containing free $P_2O_5$ precluded the determination of its liquidus surface.

Some attempt has been made to study the solidification of slags whose compositions lie along the $9Na_2O.2P_2O_5.6SiO_2$–$Na_2O.SiO_2$ section. Only half of the system has been investigated, the other half having been ascertained from the partial system shown in Fig. 23. The phase-equilibrium diagram of this section is produced in Fig. 26 in the range 0-6% $P_2O_5$. Between 1088° and 988° C. primary crystals of $Na_2O.SiO_2$ precipitate. At 988° C. the liquid is saturated not only with $Na_2O.SiO_2$ but also with $3Na_2O.P_2O_5$. That is, at 988° C. the liquid is doubly saturated, and on further cooling these two phases crystallize simultaneously. It has previously been pointed out that the orthophosphate in the partial ternary system whose section is under consideration reacts with liquid of composition $Tp_1$ (*see* Fig. 23) at 936° C. The peritectic invariant horizontal in Fig. 26 is the vertical section of the four-phase plane. At this temperature all the liquid reacts with all the orthophosphate, and below this temperature the slag becomes solid and consists of the meta-silicate and the ternary compound. Between 6·0 and 7·5 mole-% $P_2O_5$, $3Na_2O.P_2O_5$ is the primary phase, and between 7·5 and 11·8 mole-% $P_2O_5$, the ternary compound is the primary phase. Whichever the primary phase may be, $3Na_2O.P_2O_5$ appears in the binary eutectic. On the four-phase plane, however, all the orthophosphate disappears in the peritectic reaction. Crystalline slags in this section therefore contain two phases, $Na_2O.SiO_2$ and the ternary compound. Furthermore, the ternary compound, $9Na_2O.2P_2O_5.6SiO_2$, is stable up to its melting point as long as the $P_2O_5$ content of the slag in this section does not fall below 7·5 mole-%. Between 0 and 7·5 mole-% $P_2O_5$, the ternary compound decomposes to $3Na_2O.P_2O_5$ and liquid at 936° C., as formulated in equation (2).

The additive nature of the specific volumes of the eutectiferous slags has so far been demonstrated on the binary and quasi-binary sections. The variation of specific volume with the composition of a physical mixture consisting of three crystalline phases is predicted by the plane which includes the specific volumes of the three components of the system. In a ternary system such as $Na_2O$–$P_2O_5$–$SiO_2$, which consists of various partial ternary systems, the variation in specific volume is therefore determined by each individual triangle where three crystalline phases are in equilibrium. On this basis, a diagram such as that shown in Fig. 27 may be drawn. Knowing the side of the triangles and the few points within them, the iso-specific volume lines may be drawn. Within each partial ternary these lines will undoubtedly be parallel. The direction in which the planes incline

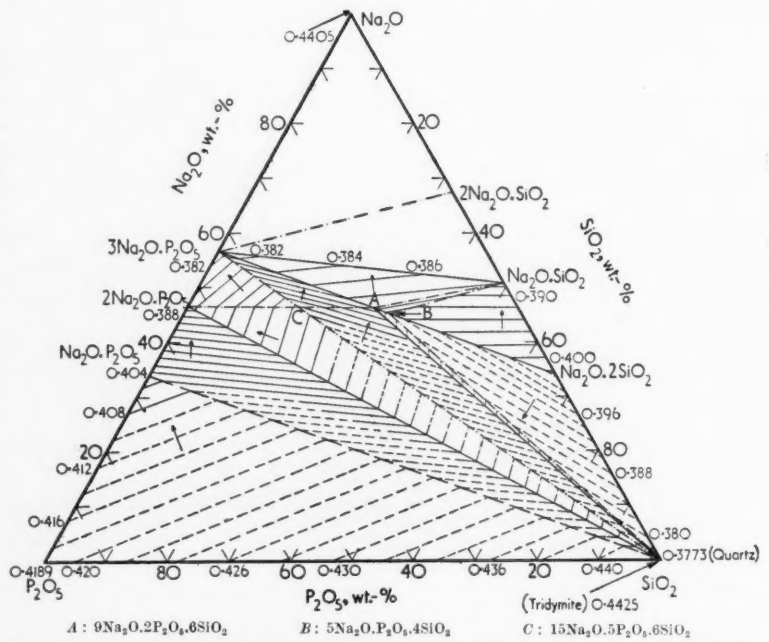



**Fig. 27—Variation of specific volumes of slags with composition in the $Na_2O$–$P_2O_5$–$SiO_2$ ternary system**

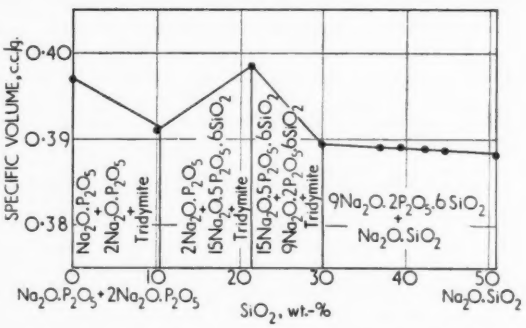



**Fig. 28—Specific volume/composition relationship**

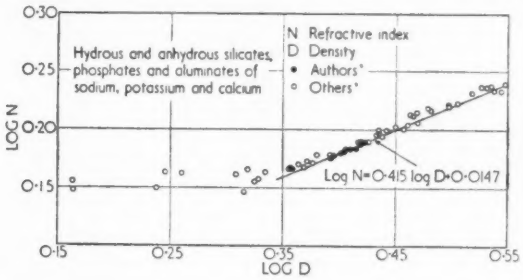



**Fig. 29—Correlation between the refractive indices and the densities of certain inorganic compounds**

is shown by an arrow. The inclination of the planes may be clarified still further by means of a vertical section through the system. The drawing in Fig. 28 represents the section that passes through $Na_2O.SiO_2$, the ternary stable compound and 40·0 wt.-% $Na_2O$ on the $Na_2O$–$P_2O_5$ binary side. The section crosses four planes : the first three intersections from the left (Fig. 28) represent the specific volumes of three-phase regions, and the fourth, which is a common line between the two partial ternaries, is that of a two-phase region. The phases for which the lines are drawn are stated in Fig. 28.

Some consideration has been given to the specific refraction of crystalline mixtures. For the present purpose, the densities and refractive indices of about 50 simple and complex compounds of hydrous and anhydrous silicates, phosphates, and aluminates of sodium, potassium, and calcium have been considered,[5] together with the author's experimental results. In Fig. 29 log $N$ is plotted against log $D$, where $N$ and $D$ are the mean refractive index and the specific gravity of the mineral respectively. Between 0·35–0·55 for log $D$ the points are located very closely to a straight line, drawn statistically. The relationship may be formulated empirically as

$$\text{Log } N = 0{\cdot}415 \log D + 0{\cdot}0147 \quad \ldots\ldots\ldots\ldots (6)$$

within the range of $D = 2{\cdot}10$, $N = 1{\cdot}42$ to $D = 3{\cdot}50$, $N = 1{\cdot}74$ ; the deviation of the calculated refractive index from the measured does not exceed $\pm 0{\cdot}015$. Within these limits it may therefore be possible to find the refractive index of a crystalline mixture if its density is known. Equation (6) may become useful in cases where the mean refractive-index measurement of a mixture is difficult.

### Acknowledgments

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# Identification of Certain Iron–Silicon Carbides

*By W. S. Owen, Ph.D., M.Eng., A.I.M., and B. G. Street, Ph.D., B.Eng.*

### SYNOPSIS

The iron–silicon carbides found by Marles, and Hurst and Riley, in rapidly cooled high-silicon cast irons have been produced in high-purity iron–carbon–silicon alloys. A new constituent, believed to be a carbide containing silicon, has been found in slowly cooled alloys containing 5–8% of silicon and small quantities of carbon. The X-ray diffraction patterns of the three carbides have been identified.

In 1910, Stead[1] found a microconstituent, associated with cementite in certain rapidly cooled white irons, which he described as silico-carbide. Many investigators have since described microconstituents supposed to be carbide containing silicon.[2, 3, 4] The subject was reviewed by Marles,[5] who carried out a systematic microscopic examination of rapidly cooled irons containing up to 7% of silicon and from 1·7% to 3·6% of carbon. A non-heat-tinting constituent was found associated with the cementite, and he

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**Table I**

**STRONGEST REFLECTIONS FROM MARLES' CARBIDE (COBALT $K_\alpha$ RADIATION)**

| $\sin^2\theta$ | $\sin^2\theta$ | $\sin^2\theta$ |
|---|---|---|
| 0·0615 | 0·2143 | 0·3169 |
| 0·1134 | 0·2211 | 0·3575 |
| 0·1299 | 0·2307 | 0·3675 |
| 0·1689 | 0·2392 | 0·3827 |
| 0·1849 | 0·2631 | 0·5526 |
| 0·1929 | 0·2829 | 0·7332 |

described this constituent as a silico-carbide. Hurst and Riley[6] have demonstrated the existence of a microconstituent containing carbon and silicon in rapidly cooled 10–15% Si alloys. More recently, a microconstituent with a duplex structure has been found by Harry[7] in very-low-carbon silicon steels (up to 0·10% C, 4% Si). He considers that one constituent of this structure is closely related to the Marles constituent. Thus, it appears that at least two carbide constituents, in addition to cementite, have been revealed by microscopic study.

This paper describes X-ray diffraction and microscopic work designed to obtain further information about the supposed iron–silicon carbides.

## EXPERIMENTAL TECHNIQUES

Much of the experimental work was performed on specimens prepared from commercially pure constituents melted and cast in air. To verify that the various structures could be obtained in high-purity alloys, some small ingots were prepared from Hilger iron *JM* 845, high-purity silicon (99·92% Si), and chemically pure graphite. These ingots were melted in recrystallized alumina crucibles under a pressure of less than $10^{-4}$ mm. of Hg, and, when necessary, were quenched through a stream of argon into cold water.

The microspecimens were polished with diamond dust, and the etching or heat-tinting techniques employed were those described by Marles and Hurst and Riley.

In the first experiments, attempts were made to isolate the silico-carbides by chemical and electrolytic methods, but in all cases the reactions resulted in decomposition of the constituents. Powders prepared by crushing solid ingots gave very broad ferrite diffraction lines together with other faint lines. Attempts to stress-relieve the powders and thus sharpen the lines were not successful, since even low-temperature annealing produced rapid graphitization. Although some information was obtained by examining the crushed powders, it became clear that diffraction patterns which could be interpreted with confidence could only be obtained from solid specimens. Back-reflection techniques, using flat film and focusing methods, proved to be unsatisfactory. The difficulties were overcome by using solid specimens (0·5–1·0 mm. dia., 1–2 cm. long) in place of the usual powder specimens, in a cylindrical 19-cm. camera of the Bradley type. These specimens were examined using filtered cobalt $K_\alpha$ radiation. Clearer diffraction patterns can be obtained by using a crystal reflection monochromator,[8] and three specimens have been examined by Dr. K. H. Jack using this technique.

The specimens were prepared by cutting a needle (approx. 2 mm. × 2 mm. × 15 mm.) from the ingot. The needle was shaped to a rough cylinder on coarse emery cloth, and was then etched to the required size. Before the final etching a flat was polished for examination by the appropriate metallographic method, to ensure that the needle was truly representative of the original ingot.

## THE CONSTITUENT REPORTED BY MARLES

Three of the alloys used by Marles in his original investigation[5] were examined. These had been prepared by melting the constituents in air and casting into a graphite mould preheated to 100° C. The microstructure, after heat tinting, of specimen *A* (2·54% C, 3·94% Si) is shown in Fig. 1. The diffraction pattern of a needle specimen from this ingot consisted of very strong broad silico-ferrite lines and clear medium-strength lines from cementite. No lines of a third structure were present. Except for a sharpening of the silico-ferrite lines, the pattern remained unchanged after annealing the specimen for 1 hr. at 650° C.

Structures of this type could be produced in high-purity vacuum-melted alloys. When the alloy contained less than 1·5% of carbon, the structure formed on slow cooling; with higher carbon contents more rapid cooling was necessary. An alloy (*B*20) containing 2·84% of carbon and 5·14% of silicon was prepared by melting the constituent elements and holding the liquid at a temperature of 1450° C. for 1 hr. in a vacuum of about $10^{-4}$ mm. of Hg, followed by cooling at a rate of approximately 35° C./min. A transverse section of the ingot showed the alloy to be white, the microstructure (Fig. 2) closely resembling that described by Marles. X-ray patterns of specimens taken from this ingot were sharp and well-defined. No lines other than those from silico-ferrite and cementite were found.

The amount of the non-heat-tinting constituent in the microstructure increases when the silicon content is increased.[5] When the alloy contains more than about 7·0% of silicon, it is possible to obtain a structure consisting of pearlite and Marles' constituent only. In the higher silicon range, two B.C.I.R.A. alloys, and two high-purity alloys melted *in vacuo* and quenched through argon into water, were examined. Their analyses were as follows:

| Specimen | Preparation | C, % | Si, % |
|---|---|---|---|
| *D* | Melted in air (B.C.I.R.A.) | 1·70 | 6·69 |
| *E* | " " " " | 1·5 | 6·2 |
| *F* | Melted *in vacuo* (high-purity) | 2·15 | 6·7 |
| *G* | " " " | 1·28 | 6·7 |

All the specimens gave diffraction patterns containing silico-ferrite lines together with a pattern different from any previously encountered. There was no detectable difference in the patterns from different specimens. The $\sin^2\theta$ values of the strongest lines are given in Table I. The reflections can be indexed by assuming the unit cell to be orthorhombic ($a \simeq 7{\cdot}89$ Å., $b \simeq 4{\cdot}60$ Å., $c \simeq 7{\cdot}20$ Å.), but this is unlikely to be the correct unit cell of the structure since the number of absent reflections would be excessive. It is most probable that the structure is of lower symmetry.

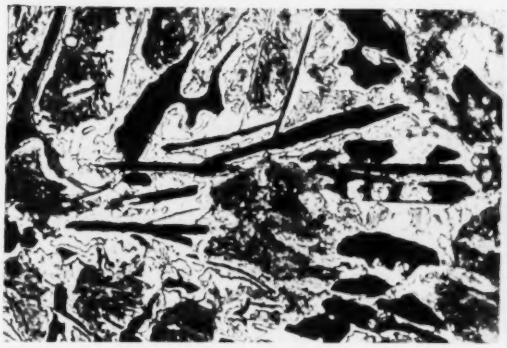

Fig. 1—Marles' alloy (specimen *A*). Etched in 4% picral and heat-tinted × 800

Fig. 2—Alloy *B*20. Etched in 4% picral and heat-tinted × 320

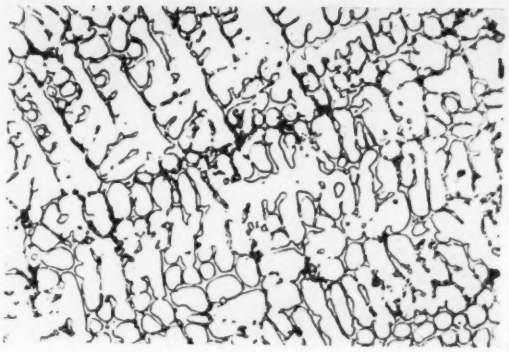

Fig. 3 — Hurst and Riley's specimen (15% Si, 0·50% C). Etched in 1 $HNO_3$ : 1 HF : 6 $H_2O$ × 600

Fig. 4 — High-purity alloy (15% Si, 0·4% C). Etched in 1 $HNO_3$ : 1 HF : 6 $H_2O$ × 3000

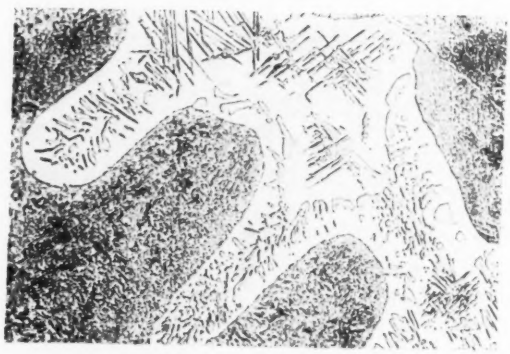

Fig. 5—Alloy *B*38. Etched in 4% picral × 250

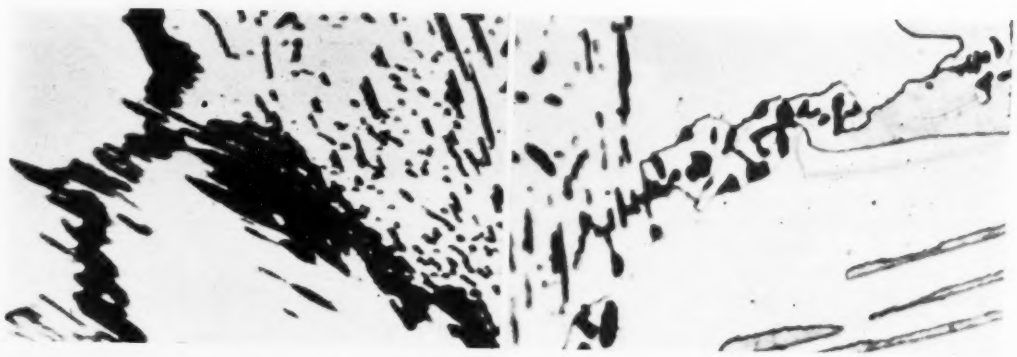

Fig. 6—Alloy *B*38. Etched in 4% picral and heat-tinted; (*a*) Showing cementite ; (*b*) showing second constituent precipitating within X-constituent × 2000

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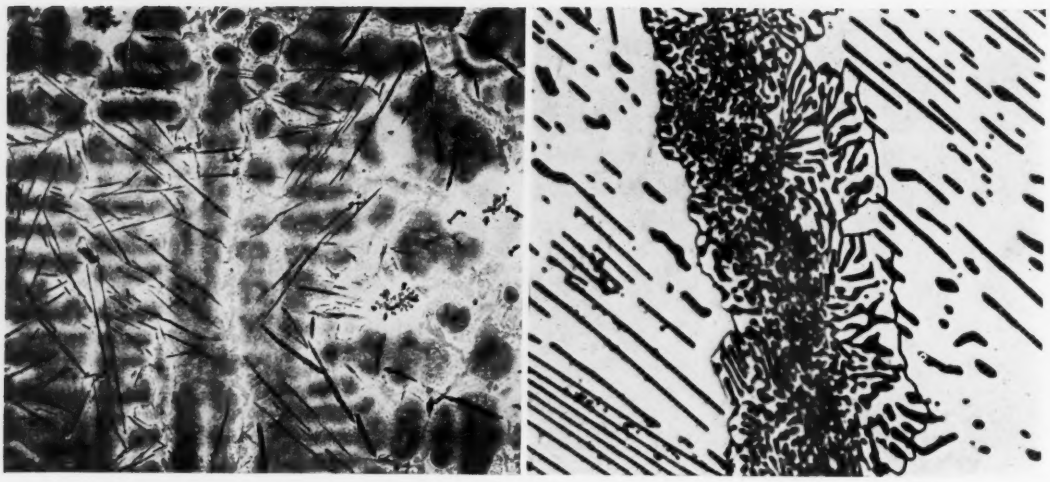

Fig. 7—Alloy *B22*. Etched in 4% picral and heat-tinted : (*a*) × 25 ; (*b*) × 2000

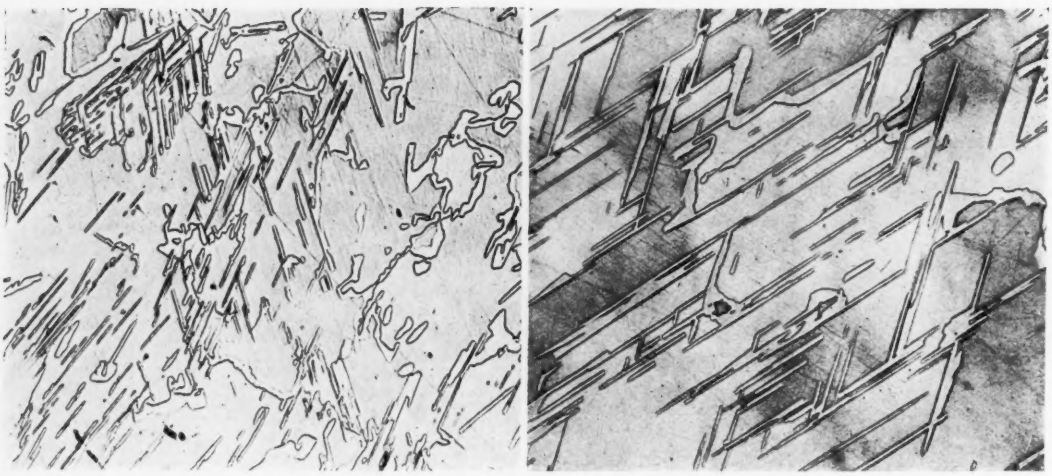

Fig. 8—Alloy *B41*. Etched in 4% picral : (*a*) × 200; (*b*) × 850

It is therefore concluded that when Marles' constituent occurs in alloys which contain more than about 6% of silicon, it can be identified by the X-ray methods which have been described. By microscopic examination the constituent can be found in alloys containing as little as 2·7% of silicon. The relatively poor sensitivity of the X-ray method may be attributed to the difficulty of detecting the weak reflections from a low-symmetry structure. In the lower silicon alloys, cementite is present both as a component of the pearlite and as a massive structure which readily heat-tints. The diffraction patterns from this constituent are identical with those of cementite extracted from annealed hyper-eutectic pure iron–carbon alloys.[9]

## THE CONSTITUENT DESCRIBED BY HURST AND RILEY

Hurst and Riley examined rapidly cooled alloys containing 10–15% of silicon and 0·16–1·00% of carbon, and, by microscopical methods, demonstrated the existence of a silico-carbide phase, which occurred as an intergranular microconstituent (*see* Fig 3). Diffraction patterns were obtained from one of their specimens and also from others prepared from high-purity vacuum-melted materials in the manner previously described (*see* Fig. 4).

All these patterns showed strong silico-ferrite lines and lines from an unknown structure that does not appear to be related to the structures found in the Marles alloys. It proved very difficult to find a unit cell which would give calculated values of $\sin^2\theta$ comparable with the measured values. The only indices that could be found were those derived from an orthorhombic cell ($a \simeq 5{\cdot}64$ Å., $b \simeq 6{\cdot}16$ Å., $c \simeq 7{\cdot}54$ Å.). Again, it seems most probable that the true unit cell is of lower symmetry. The details of the diffraction pattern are given in Table II.

## AN IRON–SILICON CARBIDE IN SLOWLY COOLED ALLOYS

Examination of a series of low-carbon high-purity alloys (*see* Table III) melted *in vacuo* and cooled at 5° C./min. revealed the existence of a new micro-constituent.

The alloy with only 0·16% of carbon consisted of small graphite nodules with islands of pearlite embedded in a silico-ferrite matrix.

The 0·75% C alloy contained more pearlite, the gross structure of which was dendritic (*see* Fig. 5).

A new constituent (for convenience called the X-constituent) was present in the silico-ferrite areas. The pearlite heat-tinted in the usual manner, the silico-ferrite was unaffected, and the X-constituent tinted to a light straw colour. The X-ray diffraction pattern of a needle from this specimen contained only

**Table II**

**STRONGEST REFLECTIONS FROM HURST AND RILEY'S CARBIDE (COBALT $K_\alpha$ RADIATION)**

| $\sin^2\theta$ | $\sin^2\theta$ | $\sin^2\theta$ |
|---|---|---|
| 0·0775 | 0·2395 | 0·5595 |
| 0·1027 | 0·2503 | 0·5694 |
| 0·1847 | 0·2783 | 0·6817 |
| 0·1912 | 0·3043 | 0·7412 |
| 0·2146 | 0·4806 | 0·7611 |
| 0·2288 | 0·5040 | |

**Table III**

**LOW-CARBON HIGH-PURITY ALLOYS**

| Alloy | C, % | Si, % |
|---|---|---|
| *B*37 | 0·16 | 5·55 |
| *B*38 | 0·75 | 5·15 |
| *B*22 | 1·02 | 5·12 |
| *B*21 | 2·02 | 5·12 |
| *B*41 | 0·46 | 8·10 |
| *B*42 | 1·00 | 7·76 |

silico-ferrite and normal cementite lines. The cementite reflections probably originated from the pearlite structure, any reflections from the X-constituent being too weak to be recorded. In some areas the X-constituent appeared as discrete rounded particles, but more frequently it formed a Widmanstätten pattern. The interdendritic silico-ferrite did not appear to be continuous with the silico-ferrite lamellae of the pearlite, and examination of the specimen at high magnifications showed that this was caused by a band of cementite which had been precipitated around the pearlite grains (Fig. 6*a*). In general, the X-constituent did not touch the boundaries of the pearlite areas. A careful examination of a large area of the specimen revealed only two points at which these microconstituents made contact. At one of these, shown in Fig. 6*b*, another constituent, with exactly the same heat-tinting characteristics as cementite, had begun to precipitate within the X-constituent. This precipitation was apparently nucleated by the cementite in the pearlite. The X-constituent surrounding the precipitated cementite was more resistant to heat-tinting than the areas in which no precipitation had taken place. No evidence of precipitation of cementite was found in any of the X-constituent needles other than those in contact with pearlite.

The general appearance of the heat-tinted microstructure of the alloy containing 1·02% of carbon is shown in Fig. 7*a*. At a few points, graphite aggregates have formed. The remainder of the structure consists of pearlite dendrites interspersed with areas of silico-ferrite in which are embedded globules and needles of the X-constituent. The pearlite areas are interlaced with black needles. These could not be distinguished from the X-constituent when the specimen was etched in 4% picral. However, examination of the heat-tinted specimen at high magnification revealed a duplex structure within the needles (*see* Fig. 7*b*). The tinted component of the duplex structure had the same appearance as the cementite in the pearlite, and at some points cementite lamellae extended into the needles. The non-heat-tinted component was not continuous with the silico-ferrite lamellae.

The specimen containing 2·02% of carbon had completely graphitized.

All the alloys of the 8% Si series were graphitized, except for the one with the lowest carbon content (8·10% Si, 0·46% C), the microstructure of which is shown in Fig. 8*a*. The same structure was produced when heat-tinting or a hydrofluoric acid etch was used. The constituent embedded in the silico-ferrite groundmass reacted to the various metallographic techniques in a similar manner to the X-constituent, and the general appearance of this

**Table IV**

**STRONGEST REFLECTIONS FROM X-CONSTITUENT (ALLOY *B*41) (COBALT $K_\alpha$ RADIATION)**

| $\sin^2\theta$ | $\sin^2\theta$ | $\sin^2\theta$ |
|---|---|---|
| 0·0723 | 0·2543 | 0·5019 |
| 0·0766 | 0·2761 | 0·5425 |
| 0·0922 | 0·2876 | 0·5538 |
| 0·1267 | 0·2993 | 0·5656 |
| 0·1640 | 0·3124 | 0·5750 |
| 0·1698 | 0·3197 | 0·5848 |
| 0·1862 | 0·3405 | 0·6144 |
| 0·1923 | 0·3694 | 0·6487 |
| 0·2061 | 0·3796 | 0·6644 |
| 0·2101 | 0·4241 | 0·6846 |
| 0·2140 | 0·4341 | 0·7118 |
| 0·2229 | 0·4592 | 0·7388 |
| 0·2300 | 0·4675 | 0·7593 |
| 0·2404 | 0·4754 | 0·8681 |
| 0·2470 | 0·4843 | |

structure was very similar to that of the interdendritic areas of the 5% Si alloys (*cf.* Figs. 5 and 8*a*). The X-constituent had precipitated at the silico-ferrite grain boundaries and in a Widmanstätten pattern within the grains (Fig. 8*b*). All the etching methods revealed heterogeneity in the silico-ferrite. The X-ray diffraction pattern from specimens cut from this ingot contained silico-ferrite lines and a pattern due to the X-constituent. This was not related to either of the iron–silicon carbides previously described. The $\sin^2\theta$ values for $CoK_\alpha$ radiation are given in Table IV. The structure appears to be isomorphous with that of a carbide from an iron–manganese–silicon–carbon alloy[10] (32% Mn, 14–15% Si). This carbide has a triclinic unit cell but can be described in terms of a slightly distorted hexagonal cell of dimensions $a \simeq 6{\cdot}4$ kX., $c/a \simeq 1{\cdot}5$.[10]

## DISCUSSION OF RESULTS

Cementite in high-silicon alloys heat-tints in a characteristic manner and gives diffraction patterns which are indistinguishable from those produced by the carbide $Fe_3C$.

The fact that the new microconstituent found in slowly cooled high-silicon low-carbon alloys is precipitated in the form of a well-defined Widmanstätten pattern indicates that it is rejected from silico-ferrite at a fairly low temperature. The solubility of carbon in silico-ferrite decreases when the temperature is reduced, and since, for example, the alloy *B*41 contained only one precipitate, it is reasonable to assume that the X-constituent is a carbide. In the vicinity of pearlite, cementite (not X-constituent) is precipitated (Fig. 6*a*), which suggests that the new carbide is less stable, but more easily nucleated, than cementite. This contention is supported by the evidence that when a needle of the X-constituent grows in such a way as to make contact with cementite particles, cementite precipitates within the X-constituent. The ability of the new constituent to precipitate cementite strongly supports the view that it is a carbide.

The diffraction pattern of the X-constituent is not related to the patterns produced by binary iron carbides. When particles of cementite are precipitated within the X-constituent needles, the parent constituent in the immediate vicinity of the precipitate becomes more resistant to heat-tinting (Fig. 6*b*), probably owing to an increase in silicon content.

Thus, it seems that the precipitation of cementite causes the rejection of silicon from the areas in which the precipitation occurs. This evidence suggests that the X-constituent contains silicon and, therefore, can be described as an iron–silicon carbide. Also, since there is no demarcation between the silicon-enriched and the unaffected areas, it seems that the X-constituent can exist with a range of silicon content.

The results obtained from an examination of the alloy *B*22 (5·12% Si, 1·02% C) indicate that this iron–silicon carbide can also be precipitated from austenite. When the surrounding austenite transforms to pearlite, the cementite precipitation reaction discussed above is nucleated and a duplex structure is formed within the original iron–silicon–carbide needles (Fig. 7*b*). This structure closely resembles the duplex microstructure found by Harry[7] in certain 4% Si steels. The present work indicates that the component of this structure that does not heat-tint is an iron–silicon carbide but is not related to the structure of Marles' constituent.

## Acknowledgments

The authors wish to thank Mr. J. E. Hilliard for providing some of the specimens and supplying the photographs shown in Fig. 7, and Dr. K. H. Jack for examining three of the specimens by special X-ray methods. They are also indebted to Mr. H. Morrogh, Dr. R. V. Riley, Dr. K. H. Jack, and Dr. S. J. Kennett, for helfpul discussions during the course of the investigation.

The British Cast Iron Research Association and the Staveley Iron and Chemical Co., Ltd., provided specimens which had been used in earlier investigations. All the specimens were analysed by the British Cast Iron Research Association.

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# Trapping of Gases in Cold-Compacted Powders

*By J. Williams, B.Sc.*


## SYNOPSIS

Investigations have been carried out into the state of the gases in cold-pressed compacts of iron and thoria powders. In iron powder, it is shown that about 80% of the gases originally present between loosely packed particles may be mechanically entrapped during compacting, the pressure of the entrapped gases increasing as the compacting pressure is raised. Effusion of these gases from the compact occurs subsequently, on standing in air, the time to attain equilibrium with the external atmosphere increasing with rising compacting pressure.

With the experimental method used for iron powder, it is not possible to distinguish mechanically entrapped gases in thoria compacts, owing to the interference of very considerable amounts of adsorbed gases. The amount of such adsorbed gas increases with time of standing before extraction. An explanation of this effect is put forward, based upon the relaxation with time of the interparticle bonding forces within the compact and the creation thereby of fresh surfaces.


## Introduction

GASES present in a metal-powder compact may influence the sintering behaviour of the compact. For example, surface films (oxide or nitride), which prevent metallic adhesion, may form by reaction of the metal powder with the gas atmosphere in the compact, or, if the entrapped gases cannot diffuse through the metal lattice in the last stages of sintering, totally enclosed pockets of gas might form and prevent complete sintering.

The chief potential sources of gas in a powder compact are :

*Gases Dissolved in the Metal Particles*—The amount and nature of these gases depend upon the method of manufacture of the powder and can be controlled, in certain cases, by heat-treatment before pressing.

*Gases Adsorbed on the Particle Surface*—Adsorbed gases are of major importance in powder metallurgy because of the large surface area/weight ratio associated with a powder. Gas adsorption on metal surfaces has been fairly extensively studied,[1] and powder samples have been used in several of these investigations.

*Gases Mechanically Entrapped during the Pressing Operation*—The possible occurrence of such a phenomenon is mentioned in the literature, and, although it has been suggested that such entrapped gases may be partly responsible for the cracking of compacts that may occur during[2] and after ejection from the die,[3] no quantitative data to support this view have been reported.

The investigation to be described was initiated to determine the extent to which gas could be entrapped under varying compacting conditions for such dissimilar materials as iron and thoria powders.

## EXPERIMENTAL DETAILS

The gases from the compacts were extracted in an evacuated glass system of known volume. The amount of gas removed from the sample was determined from observations of the pressure rise in the system, it being assumed that when equilibrium pressure is attained in the apparatus, the pressures in the voids of the compact and in the apparatus are of the same order. The subsequent quantitative interpretation of the results is not significantly affected by the small amount of gas left in the voids.

The apparatus, shown in Fig. 1*a*, consists essentially of a Torricellian vacuum of very large volume, forming part of a larger system designed particularly for the study of gas evolution during the sintering of metal powders. By means of a hand torch, the apparatus was baked out as far as rubber vacuum seals and greased taps would allow. Throughout the experiments, the vacuum conditions were arbitrarily fixed at an initial pressure of 1·5–2$\mu$ and a maximum rate of pressure rise of about 1$\mu$/hr. Higher initial vacua were not sought, as this would have afforded only a minor advantage. Compacts were introduced into the system by floating them up the large bore tube containing a barometric height of chemically cleaned and doubly distilled mercury.

The apparatus was calibrated by the introduction of known volumes of air, rendering the absolute accuracy of the pressure gauge of secondary importance. Small glass capsules of the types shown in Fig. 1*b* were prepared and used for this purpose. After chemical cleaning by the normal methods, the

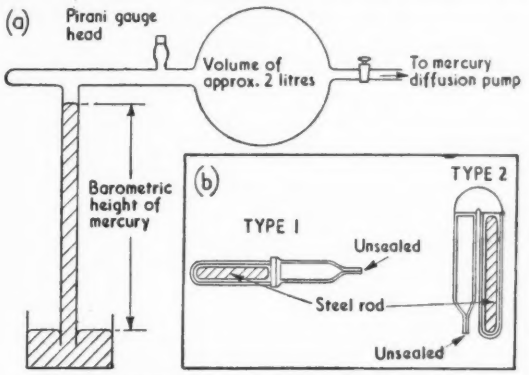


**Fig. 1—Apparatus : (*a*) General construction ; (*b*) Capsules used for calibration**

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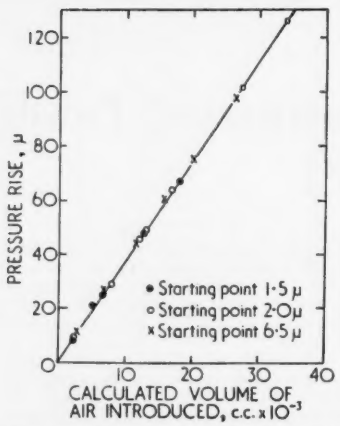


**Fig. 2—Calibration of apparatus**

open end of the capsule was placed below the external mercury surface, entrapping a volume of air equal to the initial volume of the capsule. The capsule was then allowed to rise up the mercury column. When a steady pressure had been attained, the capsule was drawn below the internal mercury surface in the column, by a magnet, and filled with mercury. The volume of the capsule, and hence the volume of air introduced, was calculated from the mass of mercury contained in the capsule. Trials showed that a pressure rise of less than 1 micron was caused by the introduction of a blank-ended capsule. The calibration was carried out in steps from three different initial pressures, and with a large number of capsules of various volumes. The results are graphically summarized in Fig. 2.

From this graph the relationship :

$$\text{Volume of air at N.T.P. (c.c.)} = \text{Pressure rise } (\mu) \times 0{\cdot}267 \times 10^{-2} \ldots (1)$$

can be derived.

## PRELIMINARY EXPERIMENTS

The first series of experiments was carried out on annealed electrolytic iron powder, for which the particle-size distribution is given in Table I. The specimens, cylindrical compacts of 0·405 in. dia., were extracted through the vertical column of mercury by a magnet, thus avoiding disturbance of the vacuum joints. No attempt was made to exaggerate the conditions for entrapment of gas in the compact, and a clearance of 0·004 in. on the diameter was allowed between plunger and die. The same die and plunger were used throughout the investigation.

**Table I**
**SUB-SIEVE SIZE ANALYSIS FOR IRON AND THORIA POWDERS**

| Percentage of Undersized Particles | Particle Size, μ | |
|---|---|---|
| | Iron | Thoria |
| 100 | 66 | 26 |
| 80 | 56 | 20 |
| 60 | 47 | 15 |
| 40 | 38 | 10 |
| 20 | 28 | 6 |
| 5 | 20 | 3 |

Specific surface area of thoria powder: $4{\cdot}75 \times 10^{-2}$ sq. cm./g.
Specific surface area of iron powder: $1{\cdot}6 \times 10^{-2}$ sq. cm./g.

A hand-operated hydraulic press was used to form the compacts, and the pressure dwell was 30 sec. The specimens were compacted axially from one end, and at four pressures—12, 22, 40, and 80 tons/sq. in. A series of compacts of various heights was formed at each pressure to give a range of pore volumes for each pressure, the greatest compact height being 0·224 in. and the least 0·026 in. These specimens were inserted into the apparatus in turn, and the equilibrium pressures were noted.

The time interval between commencement of compacting and introduction of a specimen into the apparatus was 4–5 min., this sufficing for weighing and measuring. Before each determination, the apparatus was 'blanked-off,' a minimum time of 25 min. being set for a pressure rise of the first half-micron. For specimens compacted at 12, 22, 40, and 80 tons/sq. in., it required 5, 10, 30, and 80 min. respectively to attain constant pressure in the apparatus. In this series of tests, the maximum pressure rise was 240–250 μ, and the minimum was 35μ. (Towards the upper end of the scale on the Pirani gauge, it is impossible to estimate the pressure to an accuracy of greater than ± 5μ, and this limitation is indicated by a line instead of a point on the graphs which follow.)

As any gas that is mechanically entrapped will be present in the compact pores, and any adsorbed gas

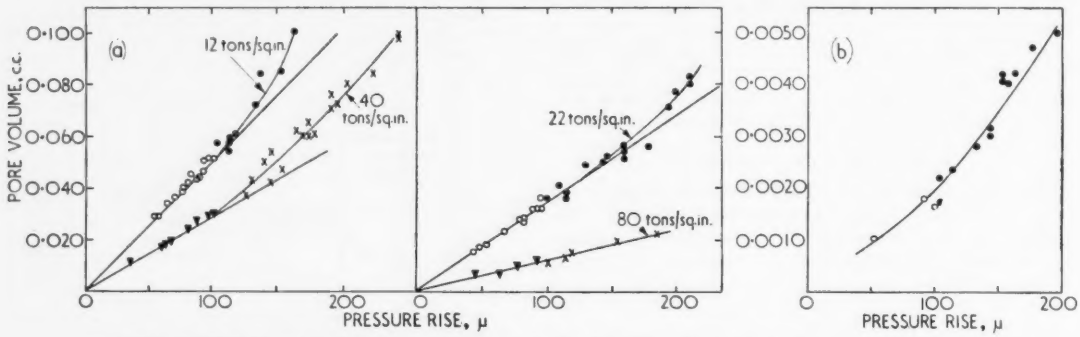


**Fig. 3—Relationship between pressure rise and pore volume : (*a*) iron ; (*b*) thoria**

## Table III

**EXPERIMENTAL VALUES FOR PRIMARY AND SECONDARY GAS EVOLUTIONS AND THE DERIVED MECHANICALLY ENTRAPPED AND ADSORBED GAS CONTRIBUTIONS***

| (i) Compacting Pressure, tons/sq. in. | (ii) Specimen No. | (iii) (iv) Primary Evolution *P* | | (v) (vi) Secondary Evolution *S* | | (vii) Pore Volume, c.c. | (viii) Original Gas *X*, c.c. | (ix) (x) Mechanically Entrapped Gas *M* | | (xi) (xii) Adsorbed Gas *A* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pressure Rise, $\mu$ | Gas Volume, c.c. | Pressure Rise, $\mu$ | Gas Volume, c.c. | | | Actual Volume, c.c. | Ratio *M*/*X* | Actual Volume, c.c. | Ratio *A*/*X* |
| 12 | S31 | 95 | 0·254 | 73 | 0·195 | 0·057 | 0·149 | 0·110 | 0·74 | 0·144 | 0·97 |
| | T31 | 110–115 | 0·294 | 80 | 0·214 | 0·057 | 0·177 | 0·137 | 0·77 | 0·157 | 0·89 |
| | U31 | 74 | 0·198 | 56 | 0·150 | 0·040 | 0·123 | 0·088 | 0·72 | 0·110 | 0·89 |
| | V31 | 80 | 0·214 | 60 | 0·160 | 0·042 | 0·125 | 0·095 | 0·76 | 0·119 | 0·95 |
| 22 | O 2 | 96 | 0·256 | 64 | 0·171 | 0·034 | 0·166 | 0·119 | 0·72 | 0·137 | 0·82 |
| | V 2 | 110–115 | 0·307 | 75 | 0·200 | 0·042 | 0·195 | 0·149 | 0·76 | 0·156 | 0·80 |
| | L 2 | 84 | 0·224 | 48 | 0·128 | 0·027 | 0·137 | 0·123 | 0·90 | 0·101 | 0·74 |
| | F21 | 150 | 0·400 | 88 | 0·235 | 0·050 | 0·236 | 0·215 | 0·91 | 0·185 | 0·78 |
| 40 | U 1 | 63 | 0·168 | 30 | 0·080 | 0·018 | 0·117 | 0·106 | 0·90 | 0·062 | 0·58 |
| | N 1 | 60 | 0·160 | 31 | 0·083 | 0·017 | 0·107 | 0·094 | 0·88 | 0·066 | 0·62 |
| | G 1 | 145 | 0·387 | 78 | 0·208 | 0·042 | 0·278 | 0·221 | 0·79 | 0·165 | 0·59 |
| | O 1 | 86 | 0·230 | 45 | 0·120 | 0·027 | 0·160 | 0·136 | 0·85 | 0·094 | 0·56 |
| 80 | X 4 | 67 | 0·179 | 21 | 0·056 | 0·007 | 0·181 | 0·130 | 0·72 | 0·061 | 0·34 |
| | U 4 | 160–170 | 0·427 | 60 | 0·160 | 0·019 | 0·366 | 0·286 | 0·78 | 0·131 | 0·36 |
| | B 4 | 95 | 0·254 | 35 | 0·093 | 0·012 | 0·229 | 0·172 | 0·75 | 0·082 | 0·36 |
| | Y 4 | 80 | 0·214 | 25 | 0·068 | 0·009 | 0·183 | 0·156 | 0·85 | 0·058 | 0·32 |

* Columns (iv) and (vi) are derived from equation (1); column (ix) is derived from equation (3), and column (i) from equation (4).

extracted will come from their surfaces, a plot of pore volumes of the compacts and their weights against pressure rise was examined. The volume of the compacts was determined from the dimensions, which were measured by micrometer to $\pm$ 0·0005 in. The pore volume is the difference between the volume as determined by dimensional measurement and the calculated theoretical volume corresponding to the weight of the compact.

The experimental results relating pore volume to pressure rise (or gas evolved) are shown in Fig. 3*a*. These graphs are reasonably straight over their lower portions, but tend to deviate with greater pore volume.

### Interpretation of Results of Preliminary Experiments

The relationship between the weight of powder $W$ and the volume of gas $X$ present in the powder voids before compacting is

$$X \text{ (c.c. at N.T.P.)} = W \text{ (g.)} \times 0{\cdot}184 \ldots\ldots\ldots (2)$$

The apparent densities of the compacts formed were constant for each compacting pressure, and the ratio pore volume to weight of compact for each pressure is detailed in Table II.

## Table II

**RELATIONSHIPS BETWEEN GAS EXTRACTED AND THAT ORIGINALLY PRESENT**

| (i) Compacting Pressure, tons/sq. in. | (ii) Pore-Volume/ Weight, c.c./g. | (iii) Pressure-Rise/ Pore-Volume, $\mu$/c.c. | (iv) Extracted Gas *E*/Original Gas *X* |
|---|---|---|---|
| 12 | 0·0630 | $1{\cdot}93 \times 10^3$ | 1·75 |
| 22 | 0·0380 | $3{\cdot}00 \times 10^3$ | 1·65 |
| 40 | 0·0290 | $3{\cdot}40 \times 10^3$ | 1·43 |
| 80 | 0·0092 | $8{\cdot}50 \times 10^3$ | 1·13 |

The relation between the pressure rise in the apparatus due to evolution of gas from the compacts and the pore volume of these compacts can be derived from the straight-line portion of the graphs of Fig. 3*a*. The results are given in column (iii) of Table II.

Combining equations (1) and (2) with columns (ii) and (iii) of Table II, the expressions in column (iv) of Table II are obtained for the gas actually extracted experimentally $E$, in terms of the amount of gas $X$ present in the powder voids before compacting.

The maximum amount of gases that could be mechanically entrapped irrespective of compacting pressure is, of course, $X$. As the gas actually extracted is in all cases greater than this, and as all experiments were conducted at room temperature, adsorbed gases must be present. Experiments were made to separate the effects of mechanically entrapped gases and adsorbed gases.

### THE MECHANICALLY ENTRAPPED GAS CONTRIBUTION

It is assumed that air will re-enter the pores when the specimen is removed from the apparatus, after the first extraction of gases, and that adsorption will again take place on the surface of the pores to the same extent as before extraction. If the specimen is subjected to a further extraction when equilibrium has been reached, the volume of gases evolved should consist of the gases that filled the pores at atmospheric pressure plus an amount of adsorbed gas equal to that evolved on the first extraction. (As is shown on p. 22, the gas entrapped in the pores in the pressed compact is at pressures considerably higher than atmospheric.)

For a primary evolution of gas $P$, secondary evolution $S$, and pore volume $V$, then :

Mechanically entrapped gas $M = P - S + V$ .....(3)

Adsorbed gas evolved $A = S - V$ .....(4)

When the first extraction had been finished, each specimen was removed from the apparatus and allowed to stand in a desiccator for 2 or 3 days before the second extraction. The results, based on various typical specimens of primary and secondary extraction, are given in Table III. In this Table, the volumes of mechanically entrapped and adsorbed gases are calculated from equations (3) and (4); they are also given in terms of the volume of gas $X$ present in the powder voids before compacting. Column (x) of Table III shows that much of the gas originally present in the powder interspace (about 80%) is mechanically entrapped during compacting.

Using an average of 80% of the originally present gas entrapped, it can be calculated that, assuming no increase in adsorption due to the increased pressure of gas, the mechanically entrapped gas pressure is approximately 2·5, 4, 5, and 15·5 atm. for compacts formed at 12, 22, 40, and 80 tons/sq. in. respectively. Here and elsewhere the term ' mechanically entrapped gas ' refers to the gas present in the compact when extraction was started.

## THE ADSORBED GAS CONTRIBUTION

Table III gives the amounts of adsorbed gas as a function of the original amount of gas $X$ present in the uncompacted powder. It will be seen that this function diminishes in value as the compacting pressure rises. A correlation was therefore attempted between the amount of adsorbed gases obtained experimentally and that evolved from the pore surface as calculated from the density of the compacts formed at the various pressures.

Working on the premise that the adsorbed gases are evolved from the pore surfaces, it is possible to calculate the manner in which this factor would be expected to vary with density. Two simplifying assumptions must be made :

(i) The total number of pores $N$ originally present in the uncompacted powder filling the die space remains constant, independent of compacting pressure

(ii) The pores are of equal size, and do not change shape during compacting, so that the volume is a cubic function of some parameter (the equivalent radius) and the surface area is a squared function of the same parameter.

For a given weight of powder $W_p$ compacted to a density $D_p$ under a given pressure $P$ :

$$V_p = \frac{W_p}{D_p} - \frac{W_p}{D_T}, \quad \text{.....(5)}$$

where $V_p$ = volume of pores, and $D_T$ = theoretical density of the powder particles.

For uncompacted powder of weight $W$, considering the equivalent pore radius $r_o$ :

$$V_o = Nk_1r_o^3, \quad \text{.....(6)}$$

where $k_1$ is a constant converting $r_o^3$ to volume. Also, from equation (5) :

$$V_o = W_p\left(\frac{1}{D_o} - \frac{1}{D_T}\right) = Nk_1r_o^3 \quad \text{.....(7)}$$

where $D_o$ is the bulk density of the powder.

If a weight $W_p$ of powder is compacted to a density $D_p$ and the equivalent radius changes to $r_p$, then :

$$V_p = W_p\left(\frac{1}{D_p} - \frac{1}{D_T}\right) = Nk_1r_p^3 \quad \text{.....(8)}$$

Dividing equation (8) by equation (7) :

$$\frac{r_p^3}{r_o^3} = \frac{\frac{1}{D_p} - \frac{1}{D_T}}{\frac{1}{D_o} - \frac{1}{D_T}} \quad \text{.....(9)}$$

All the terms on the right-hand side are known, so that $r_p$ can be obtained as a function of $r_o$.

The surface area $A$ of the pores of uncompacted powder is given by : $A_o = Nk_2r_o^2$ .....(10)
where $k_2$ is a constant converting $r_o^2$ to area.

For the compacted powder :

$$A_p = Nk_2r_p^2 \quad \text{.....(11)}$$

Dividing equation (11) by equation (10) :

$$\frac{A_p}{A_o} = \frac{r_p^2}{r_o^2} \quad \text{.....(12)}$$

Combining equations (12) and (9), it is possible to obtain a value for the pore surface area (which is the adsorbing surface also) of a compact, in terms of that for the uncompacted powder. Calculations were made for samples compacted at the various pressures used, and the results are given in Table IV.

Taking this value and assuming that the amount of adsorbed gas is directly proportional to an adsorbing surface, the corresponding ratio $A/X$ for the other pressures can be calculated. The results of observed values of $A/X$ (from column (xii) of Table III) and the calculated values are given in Table V. These show that, despite the assumptions made, a reasonable correlation exists between the experimental values for the adsorbed gas and those calculated from density measurements.

The experimental results show that the amount of adsorbed gas extracted forms an appreciable proportion of the total (mechanically entrapped and adsorbed). It is known that the amount of gas adsorbed on a metal surface is proportional to the square root of the gas pressure above the surface.

### Table IV

### SURFACE AREA RATIOS CALCULATED FROM COMPACT DENSITIES

| Compacting Pressure, tons/sq. in. | Density, g./sq. cm. | Pore Radius $r_p$ / Pore Radius $r_o$ | Surface Area $A_p$ / Surface Area $A_o$ |
|---|---|---|---|
| 0 | 3·21 | 1·00 | 1·00 |
| 12 | 5·30 | 0·68 | 0·46 |
| 22 | 6·00 | 0·59 | 0·35 |
| 40 | 6·35 | 0·54 | 0·29 |
| 80 | 7·35 | 0·36 | 0·13 |

### Table V

### COMPARISON OF CALCULATED AND OBSERVED RATIOS OF SURFACE AREA TO ADSORBED GAS

| Compacting Pressure, tons/sq. in. | Calculated Value of $A/X$ | Observed Value of $A/X$ from Table II |
|---|---|---|
| 12 | 0·93 | 0·93 |
| 22 | 0·79 | 0·71 |
| 40 | 0·59 | 0·59 |
| 80 | 0·35 | 0·28 |

This probably accounts for the deviation of the graphs (Fig. 3*a*) from a straight line at a higher equilibrium pressure ; as this latter increases, so the amount of adsorbed gas extracted will fall, giving rise to the lower readings observed.

## EFFUSION OF ENTRAPPED GASES WITH TIME

Gases that are mechanically entrapped in the compact at pressures of the order deduced on page 22 will probably tend to effuse with time. This can afford a check upon the conclusions already reached. A series of specimens was therefore prepared at each of the compacting pressures used in the previous experiments, and then allowed to stand in a desiccator for various times before gas extraction was carried out. For each set of specimens, the dimensions were kept constant to within 0·001 in., the same amount of powder being weighed out for each compact. After a primary extraction, each compact was removed to a desiccator and allowed to stand for 48 hr., when a secondary extraction was carried out. The results of these experiments are given in Table VI.

In all cases, the secondary evolutions remain sensibly constant, as would be expected from the previous work, whereas the primary evolutions fall with increasing time lapse, to reach a value equal to that of the secondary evolutions. This behaviour is consistent with the presence in the compact of mechanically entrapped gas, which effuses with time. Under atmospheric pressure, the major part of the mechanically entrapped gas is released in less than 30 min. from the compacts formed at 12 tons/sq. in., in 1–2 hr. from those formed at 22 tons/sq. in., and in approx. 17 and 21 hr. respectively from compacts pressed at 40 and 80 tons/sq.in.

## GASES PRESENT IN COLD-COMPACTED THORIA POWDER

Iron of the high degree of purity associated with electrolytically prepared powder is a soft, ductile material. On compacting the powder, these properties lead to ready deformation of the particles, which facilitates the mechanical entrapment of gases. Hard brittle materials (in which a lesser effect would be expected) form only relatively weak compacts ; this was a drawback when the mechanical entrapment of gases as a result of compacting such a material was investigated. The metallic carbides are usually mixed with a binder, to give mechanical strength to the green compact, but it was anticipated that the presence of the binder would complicate the interpretation of any results obtained. Refractory oxides were therefore considered, and of these it was decided to use thoria, which forms reasonably strong compacts over a limited range of compacting pressures.

Manipulation of the thoria compacts inside the apparatus by a magnet was achieved by enclosing them in a closed coil of piano wire (23 S.W.G.). A minimum thickness was imposed on the thoria specimens finally used, as the individual turns of the coil had to be spaced so as to enable mercury to get inside and surround the specimens. The specimen could slip out of the coil if its thickness were too small. It was found that the introduction of such a coil into the apparatus caused a pressure rise of only 1–3μ.

**Table VI**

**THE EFFECT OF TIME LAPSE PRIOR TO EXTRACTION, UPON THE PRIMARY AND SECONDARY GAS**

| Compacting Pressure, tons/sq. in. | Time Lapse, min. | Pressure Rise, μ | |
|---|---|---|---|
| | | Primary Extraction | Secondary Extraction |
| 12 | 5 | 90 | 60 |
| | 30 | 65 | 61 |
| | 60 | 69 | 67 |
| | 90 | 67 | 65 |
| | 120 | 67 | 64 |
| | 135 | 64 | 60 |
| 22 | 5 | 105-110 | 75 |
| | 30 | 90 | 75 |
| | 60 | 90 | 70 |
| | 120 | 70 | 70 |
| | 190 | 70 | 68 |
| | 235 | 70 | 68 |
| 40 | 5 | 66 | 35 |
| | 30 | 64 | 35 |
| | 60 | 64 | 37 |
| | 120 | 55 | 36 |
| | 180 | 43 | 40 |
| | 280 | 42 | 37 |
| | 17 hr. | 37 | 36 |
| 80 | 5 | 87 | 32 |
| | 60 | 47 | 32 |
| | 120 | 37 | 28 |
| | 360 | 37 | 30 |
| | 21 hr. | 32 | 30 |

Preliminary experiments were carried out with thoria compacts formed in the same die as that used for the iron powder. It was found that a compact 0·030 in. thick, pressed at 60 tons/sq. in., gave a pressure rise of 350μ on extraction. Pressure measurements above 200μ are undesirable (for reasons previously mentioned), and it was not practicable to reduce the thickness of compact. The cross-sectional area was therefore reduced until a convenient size was reached. This was 0·01 sq. in. and a height not greater than 0·120 in.

The compacts were formed in a carbide-lined die, using a carbide-tipped plunger, and applying a pressure of 67 tons/sq. in. from one end. Specimens of density approx. 7·2 g./c.c. were thus obtained. The height of the compacts was varied to give a range of void volumes, and extractions were carried out as described on page 20. Experimental results of pressure rise against pore volume of the compact are given in Fig. 3*b*. Greater scatter of results is obtained with thoria compacts than with iron compacts ; this is probably attributable to the relative scale of the experiments—the largest volume of thoria specimen used was 0·0177 c.c., compared with 0·477 c.c. for the iron compacts.

The form of Fig. 4 (pore volume *versus* pressure rise) is substantially the same as that obtained for iron powder. Assuming the gases to be present at atmospheric pressure in the voids of the compacts, then, for example, a void volume of 0·003 c.c. will give a pressure rise of only 1μ, whereas, in fact, a rise of 140–145μ is obtained. The compression ratio for the

**Table VII**
**GAS ADSORPTION BY THORIA COMPACTS**

| Specimen No. | Weight, g. | Pore Volume, c.c. | Primary Evolution, μ | Secondary Evolution, μ |
|---|---|---|---|---|
| 1 | 0·124 | 0·0049 | 195–200 | 220–230 |
| 2 | 0·116 | 0·0047 | 175–180 | 210–220 |
| 3 | 0·080 | 0·0032 | 140–145 | 190–195 |
| 4 | 0·084 | 0·0030 | 140–145 | 185–195 |
| 5 | 0·072 | 0·0026 | 125–130 | 165–170 |
| 6 | 0·057 | 0·0024 | 110–115 | 150–155 |
| 7 | 0·057 | 0·0022 | 100–105 | 140–145 |
| 8 | 0·049 | 0·0018 | 96–97 | 115–120 |

thoria is approx. 2·5 : 1 at the pressure used, and calculation shows that, even assuming that all the air originally present in the pores has been entrapped by the process, the volume of gas would be only 0·021 c.c. This would yield a pressure rise of 7μ in the apparatus. It is therefore obvious that the effects observed are due almost exclusively to adsorbed gases. The considerations already given would lead to the supposition that if any gases were mechanically entrapped, they would be at pressures lower than those existing in comparable iron compacts.

### GAS ADSORPTION BY THORIA COMPACTS WITH TIME

Although it appeared that the method used for iron powder was unable to distinguish effects due to mechanically entrapped gases, secondary extractions for thoria were carried out after 2 days In all cases, higher pressure rises were obtained than for the primary extraction (*see* Table VII).

The secondary extraction figures were not increased by lengthening the time of standing to 3 or 4 days. As a further check upon this apparently anomalous effect, a series of identical specimens was formed, and increasing periods of time were allowed to elapse before the primary measurements were taken. The results were as follows :

| Time Lapse, hr. | Pressure Rise, μ | |
|---|---|---|
| | Primary | Secondary |
| 0 | 155–165 | 190–195 |
| 1 | 155–160 | 190–195 |
| 2 | 160–165 | 195–200 |
| 24 | 195–200 | 195–200 |

These further results show that as the time lapse prior to primary extraction increases, so does the amount of gas evolved, reaching an ultimate figure equal to that obtained by secondary extractions.

There are two possible explanations of the effects obtained experimentally. The increase in the amount of evolved adsorbed gases with time could be due to an increase with time of the adsorbing surface area within the compact. This would necessitate some relaxation of the bonding forces between particles, and separation of the particles sufficient to allow entry and adsorption of gas at the separated surfaces. A second explanation is that the amount of adsorbed gases remains constant, but the forces holding them to the surface are in some manner increased by the compacting process. As these forces decrease with time, the amount of gas available for evolution would increase.

A compact was prepared and a primary extraction of 110–115μ was observed. If the second theory is correct, then when a specimen is allowed to remain in the apparatus for a further 2 days, the pressure should rise to that of the secondary extraction, plus any rise due to minor leaks. After 2 days' standing in the apparatus, the pressure had risen to 120–125μ. The specimen was removed to stand for a further 2 days in the atmosphere. During this latter time the pressure in the apparatus rose a further 10μ, which shows that no further gas was evolved after primary extraction. A pressure rise of 150μ was obtained on secondary extraction of this specimen. The evidence is therefore in favour of the theory postulating a relaxation of bonds within the compact, and a consequent increase of internal surface area. Such relaxation should be associated with a decrease in compact strength, but reduction in strength could not be detected because of the original mechanical weakness of the thoria compacts.

### CONCLUSIONS

It has been established experimentally that for iron powder cold-compacted at various pressures, amounts of gas, constituting in volume the major portion of the air present between the uncompacted powder particles, are mechanically entrapped. This can lead to the development of appreciable gas pressures within the compact, the pressure developed being a function of the compacting pressure. The gases entrapped in this manner slowly effuse with time and the time taken to reach equilibrium lengthens with increase of compacting pressure.

Adsorbed gases comparable in quantity to those mechanically entrapped were evolved under low pressures at room temperatures. An approximate correlation was obtained between experimentally observed values for the adsorbed gas and those derived from density determinations.

With thoria powder, the experimental method used for iron did not distinguish the effect of mechanically entrapped gas from that of adsorbed gas because of the large amounts of the latter.

Thoria compacts, on standing, adsorb further quantities of gas with time. This can be explained on the assumption that an increase of the adsorbing surface occurs by reason of relaxation of the interparticle forces, the slight separation of these particles allowing entry of gas to these fresh surfaces.

### Acknowledgments

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# PROCEEDINGS OF THE INSTITUTE

REPORTS OF COUNCIL - OFFICIAL NOTICES

## ANNUAL GENERAL MEETING, 1952

THE EIGHTY-THIRD ANNUAL GENERAL MEETING OF THE IRON AND STEEL INSTITUTE was held in London on Wednesday, 30th April, and Thursday, 1st May, 1952, the morning session on 30th April at the Royal Institution, Albemarle Street, W.1, and the other sessions at the Offices of the Institute. Mr. RICHARD MATHER, the Retiring President, was in the Chair at the beginning of the Meeting, his place thereafter being taken by Captain H. LEIGHTON DAVIES, C.B.E., the new President.

Sessions were held at 9.45 A.M. and 2.30 P.M. on Wednesday and at 10 A.M. and 2.15 P.M. on Thursday, a buffet luncheon being provided on both days in the Library of the Institute. On the Wednesday evening a Members' Dinner was held at Grosvenor House, Park Lane.

The minutes of the previous meeting were taken as read, confirmed, and signed.

### DEATH OF H.M. KING GEORGE VI

The **President** (Mr. Richard Mather), before opening the formal proceedings, referred to the death since the previous meeting of H.M. King George VI. His Majesty had been Patron of the Institute since his accession to the throne, continuing the practice of his predecessors since King Edward VII, who had become Royal Patron of the Institute 50 years ago. The Address which the Council sent to Queen Elizabeth II had been printed in the *Journal*, together with the gracious acknowledgment of that Address.

The **President** went on to express the hope that Queen Elizabeth II might have a long, happy, and prosperous reign. He announced that the Council had decided to request Her Majesty to be pleased to become the Patron of the Institute.

He also announced the deaths of Mr. W. J. Brooke and Sir Andrew Duncan since the previous meeting.

The **President** then welcomed the members and visitors, who included Dr. Oberegger, President of the Austrian Iron and Steel Institute, who had been the leading spirit in organizing the successful visit of the Institute to Austria in September, 1951.

He also referred to the forthcoming visit of the Institute to Wales, initiated by Captain Leighton Davies and his colleagues in the leading companies of South Wales.

### PRESENTATION OF REPORT OF COUNCIL AND STATEMENT OF ACCOUNTS FOR 1951

The **President** then presented the Report of Council and Statement of Accounts for 1951, to be published in the May issue of the *Journal*, and moved their adoption. He said that, both financially and in other ways, 1951 had been a very successful year. He referred in particular to the important Symposium on High-Temperature Steels and Alloys for Gas Turbines, and to the active collaboration maintained with the affiliated local societies, whose number had been increased since the beginning of the year by the affiliation of the North Wales Metallurgical Society.

Good relations had been maintained between the Institute and the British Iron and Steel Research Association, the Institute of Metals, the Institution of Metallurgists, and many other similar societies in this country and overseas.

He also spoke of the Institute's work in connection with metallurgical education, undertaken in conjunction with the other leading metallurgical institutions. The Joint Committee on Metallurgical Education was following up its earlier activities by recommending an extensive organization of facilities for metallurgical education, with particular reference to education at technical colleges and schools, and would publish a report later in the year.

The **Hon. Treasurer** (Mr. James Mitchell), who seconded the motion, said that the expenditure on general administration had changed very little from the previous year. There had been some rise in administrative expenses, due partly to the cost of the High-Temperature Symposium, and also for one or two other reasons. There was an apparent credit balance from publications of about £14,000. The solvency of the Institute depended a great deal on the *Journal*, and particularly on its advertising section ; even with the steadily rising cost of printing and paper, it should just be possible to maintain the present position. There was an excess of income over expenditure, when certain non-recurring items had been dealt with, of £718.

The motion was carried unanimously.

### PRESENTATIONS

The **President** then made the following presentations :

**The Bessemer Medal** for 1952 to Mr. H. H. Burton, C.B.E., of the English Steel Corporation, Ltd., for his distinguished services to the steel industry and to metal-

lurgy, with particular reference to the development of alloy steels and of heavy forgings.

**The Sir Robert Hadfield Medal** for 1952 to Dr. L. Reeve, of the Appleby-Frodingham Steel Company, in recognition of his contributions to the science and practice of ferrous metallurgy, and, in particular, his researches on the weldability of low-alloy steels.

**The Williams Prize** for 1951 jointly to Mr. J. A. Bond (Appleby-Frodingham Steel Company) and Mr. T. Sanderson (Workington Iron and Steel Company) for their paper on "Full-Scale Blast-Furnace Trials," published in the *Journal* for May, 1951.

Finally, the **President** made a presentation to Mr. **Richard Elsdon,** a member of the staff of the Institute since 1903, and Librarian since 1908, of a cheque subscribed to by Members on his retirement in 1951. The Council had nominated Mr. Elsdon to be an Honorary Member of the Institute, and proposed to arrange for a portrait of him to be painted and hung in the Library.

## ANNOUNCEMENTS

The **Secretary** (Mr. K. Headlam-Morley) made the following announcements :

**Changes on the Council** since the last General Meeting, in November, 1951 :

*Hon. Vice-President*—Mr. W. B. Baxter, C.B.E.

*Vice-President*—Sir Charles Bruce-Gardner, Bt.

*Member of Council*—Mr. E. Julian Pode.

*Honorary Members of Council* during their periods of office :

Mr. H. Allison, President of the Manchester Metallurgical Society, in place of Mr. A. B. Ashton.

Mr. E. W. Colbeck, President of the Sheffield Metallurgical Association, in place of Mr. E. T. Gill.

Mr. G. Baker, O.B.E., President of the Sheffield Society of Engineers and Metallurgists, in place of Professor H. W. Swift.

Mr. W. Regan, President of the Staffordshire Iron and Steel Institute, in place of Mr. K. H. Wright.

Mr. E. Taylor-Austin, Chairman of the North Wales Metallurgical Society.

In addition, at a meeting of the Council held the previous day, Mr. C. R. Wheeler, C.B.E., had been elected a Vice-President and Mr. B. Chetwynd Talbot a Member of Council.

*Retiring Members of Council*—In accordance with Bye-law 10, the names of the following Vice-Presidents and Members of Council had been announced at the Autumn Meeting, 1951, as being due to retire at the present Annual Meeting :

*Vice-President*—Mr. G. H. Latham, Mr. J. Sinclair Kerr, and Mr. H. H. Burton, C.B.E..

*Members of Council*—Dr. J. W. Jenkin, Mr. W. F. Cartwright, Mr. F. Saniter, Mr. T. Jolly, and Mr. R. A Hacking, O.B.E.

No other members having been nominated up to one month previous to the present meeting, the retiring Vice-Presidents and Members of Council were presented for re-election and declared by the **President** to be duly re-elected.

**Andrew Carnegie Scholarship**—Since the previous General Meeting, an award (second grant) had been made to Mr. B. Cina (Sheffield University) for research on the effect of cold work on the gamma–alpha transformation characteristics of three Fe–Ni–Cr steels.

**Future Meetings**—A special meeting would be held in Swansea from 7th to 9th October, 1952. A circular would be issued in due course.

The Autumn General Meeting would be held in London on 26th and 27th November, 1952.

## BALLOT FOR THE ELECTION OF MEMBERS

Dr. **L. Reeve** and Mr. **J. A. Bond,** who were appointed scrutineers of the ballot, reported that the following candidates had been duly elected :

### Members

**Agosti,** Giorgio, D.Eng. (Milan, Italy) ; **Albert,** Werner, Dr, Ing. (Solingen-Ohligs, Germany) ; **Alexander,** Mark Alexander. A.M.I.Mech.E. (Sheffield) ; **Anselmetti,** Gian Carlo (Turin, Italy) ; **Asbeck,** Gustav, Dr.Ing. (Düsseldorf-Rath, Germany); **Asbeck,** Kurt, Dr. Ing. (Düsseldorf-Rath, Germany) ; **Balfour,** Rt. Hon. The Earl of (Musselburgh) ; **Bedford,** Tom (Bournemouth) ; **Beinlich,** J. J., B.S. (Pittsburgh, Pa., U.S.A.) ; **Bergstrom,** Erik Viktor (Stockholm, Sweden) ; **Bolgiani,** Armando, Dr.Ing. (Bolzano, Italy) ; **Bruce-Gardner,** B. C., M.A. (Scunthorpe) ; **Bull,** Henry C. (London) ; **Chase,** Philip W., B.S. (Pittsburgh, Pa., U.S.A.) ; **Chatterton,** John Victor, A.I.M. (Birmingham) ; **Course,** Leonard George Odell (Bournemouth); **Demaine,** Harry (Rotherham) ; **Dunlop,** Samuel Hamilton (West Hartlepool) ; **Eimermann,** Georg (Bochum, Germany) ; **Elwell,** Edward Thomas (Wednesbury) ; **English,** Ray H., B.S. (Blawnox, Pa., U.S.A.) ; **Fielden,** Graham William Richard, B.Sc. (Manchester) ; **Fields,** Ernest Edwin (Cardiff) ; **Firth,** L. Graham (Walsall) ; **Fitzpatrick,** Christopher (Haulbowline, Co. Cork, Ireland) ; **Fitzwilson,** C. H., Jr., B.S. (San Francisco, Cal., U.S.A.) ; **Fry,** Adolf, Prof. Dr.Ing. (Lübeck, Germany) ; **Gall,** Montagu Hubert Wilson, A.M.I.Mech.E. (London) ; **Gamba,** Mario, Dr. (Milan, Italy) ; **Garland,** John, A.I.M. (Nottingham) ; **Gianola di GioBatta,** Cornelio (Milan, Italy) ; **Gibson,** Stanley (Rotherham) ; **Goodreid,** Desmond H. (Darlaston) ; **Grundy,** Thomas Arthur (Leeds) ; **Harten,** Karl Peter, Dipl.Ing. (Düsseldorf, Germany) ; **Herrmann,** Curt, Dr.Ing. (Duisburg, Germany) ; **Hey,** Roland James, B.Sc., A.I.M. (Middlesbrough) ; **Higgens,** Cecil Cyprian, A.M.I.E.E. (Doncaster) ; **Hillman,** Bernard Houndle (Düsseldorf, B.A.O.R. 4) ; **Hofmeister,** Hans (Duisburg, Germany) ; **Houdremont,** Eduard, Prof. Dr.Ing. (Essen-Bredeney, Germany) ; **Hughes,** William (Vanderbijl Park, South Africa) ; **Jump,** Peter Alexander Edward (Sheffield) ; **Kerl,** Ernst (Pretoria, South Africa) ; **Kerr,** David Malcolm (Glasgow) ; **Keys,** Lewis Henry (Farnborough, Hants) ; **King,** David Walter (London) ; **Köster,** Werner, Prof. Dr.Phil. (Stuttgart, Germany) ; **Kristoffersen,** Kristoffer, Dr.Techn. (Oslo, Norway) ; **Kügel,** Ernst E. (New York, N.Y., U.S.A.) ; **Lindblom,** Yngve (Stockholm, Sweden) ; **McArdle,** Gordon Dickinson (Middlesbrough) ; **Masgeik,** Wilhelm (Duisburg, Germany) ; **Masi,** Oscar, Dr. (Milan, Italy) ; **Mather,** William Harvey, Lt.-Col., O.B.E., T.D., A.M.I.Mech.E., A.M.I.E.E. (Middlesbrough) ; **Mathur,** Prem Saran, B.Sc.Met. (Duisburg-Wanheim, Germany) ; **Meller,** Karl (Cologne, Germany) ; **Minnis,** Herbert, B.A. (Pittsburgh, Pa., U.S.A.) ; **Morris,** Charles Evan Henry (Port Talbot) ; **Mossoux,** Roger Victor Désiré Joseph (Herstal-lez-Liège, Belgium) ; **Münker,** Friedrich (Duisburg, Germany) ; **Newman,** Frank Eric (London) ; **Osment,** Bernard David John, B.Sc., F.I.M., F.R.I.C., A.M.I.M.M. (Newcastle-on-Tyne) ; **Petch,** Norman James, B.Sc., B.Met., Ph.D. (Leeds) ; **Pourbaix,** Marcel, Dr. (Brussels, Belgium) ; **Powell,** John Harford (Margam) ; **Power,** Ellen, M.A. (Dublin) ; **Powers,** Arthur Eugene, Ph.D., B.S. (Schenectady, N.Y., U.S.A.) ; **Price,** William Oswald Weeks, B.Sc. (Llanelly) ; **Rassbach,** Herman Philip, B.Sc. (Chicago, Ill., U.S.A.) ; **Redmore,** George Arthur James, (Port Talbot) ; **Rees,** Howard Treseder, J.P. (Cardiff) ; **Reimann,** Martin (Wuppertal-Langerfeld, Germany) ; **Rivoira,** Luigi, Dr. (Turin, Italy) ; **Rodham,** Eric J. (Lidcombe, N.S.W., Australia) ; **Rohland,** Walter, Dr.Ing. (Krefeld, Germany) ; **Scariolo,** Francesco, D.Eng. (Milan, Italy) ; **Schemann,** Wilhelm Frank (Gelsenkirchen, Germany) ; **Schlacher,** Hans, Dipl.Ing. (Bruck a.d.Mur, Austria) ; **Schneider,** Carl Heinrich Ludwig (Mülheim-Speldorf, Germany) ; **Schüller,** Josef (Duisburg, Germany) ; **Springorum,** Friedrich Alfred, Dipl.Ing. (Duisburg-Huckingen, Germany) ; **Steck,** Alfred B., B.S. (Everett, Mass., U.S.A.) ; **Taljaard,** Petrus Arnoldus, B.Sc. (Vanderbijl Park, South Africa) ; **Taylor,** Fred (Oldham) ; **Vandestrick,** Franz A. (Liège, Belgium) ; **Vold,** Ole Ingier,

B.S. (Bergen, Norway); **Waddell,** Albert Victor (London); **Waltl,** Hans, Dipl.Ing. (London); **Watkins,** J. G., M.A., Wh.Sc., A.M.I.Mech.E. (Sheffield); **Weiss,** Bernhard (Dahlbruck u. Kreutztal, Germany); **Wessendorf,** Gerhard (Höhenlimburg, Germany); **Wever,** F., Professor Dr. (Düsseldorf, Germany); **Weyel,** Otto-Arthur, Dr.Ing., Dipl. Ing. (Hagen-Haspe, Germany); **Wick,** Wolfgang, LL.D., D.Econ. (Radenthein, Austria); **Wimmer,** Anton, Dr.Ing. (Höhenlimburg, Germany); **Wolverson,** Thomas (Bilston); **Wrba,** Max, Dr.Ing., Dipl.Ing. (Düsseldorf, Germany); **Wright,** Eleanor V., A.B. (Detroit, Mich., U.S.A.).

### Associate Members

**Ainslie,** Alan (Newcastle-on-Tyne); **Allison,** Dennis Fenwick (Newcastle-on-Tyne); **Bankier,** Alexander Martin (Newcastle-on-Tyne); **Barfield,** Clifford John (Hatfield); **Bassett,** Keith Terence (Newcastle-on-Tyne); **Bigg,** Anthony Philip (Newcastle-on-Tyne); **Bindley,** David (Bournemouth); **Bullock,** Bernard (Birmingham); **Clark,** Derek Foster (Corby); **Cowlishaw,** Frank Reginald (Birmingham); **Dales,** Arthur (Newcastle-on-Tyne); **Dickson,** Michael (Corby); **Ewing,** John F., M.S. (Ann Arbor, Mich., U.S.A.); **Gane,** Nicholas (Newcastle-on-Tyne); **Garstone,** John (Sheffield); **Gaskell,** Philip Darwin (Newcastle-on-Tyne); **Gibbon,** Ronald Bryan (Newcastle-on-Tyne); **Hardwick,** Allan Terence, (Middlesbrough); **Harle,** Cyril D. (Workington); **Harries,** Donald Rees, B.Sc. (Cambridge); **Holmes,** Wilbur G., M.S. (Ann Arbor, Mich., U.S.A.); **Horton,** Frank George, L.I.M. (Wolverhampton); **Howd,** Derrick (Newcastle-on-Tyne); **Keith,** Robert Eugene, M.S. (Ann Arbor, Mich., U.S.A.); **Kiessel,** William R., M.S.E. (Ann Arbor, Mich., U.S.A.); **Kiukkola,** Kalevi Viljam, B.Sc. (Pittsburgh, Pa., U.S.A.); **Lancaster,** John Darrell (Newcastle-on-Tyne); **Leitch,** Daidh (Glasgow); **Lumb,** William (Sheffield); **Mavrocordatos,** Demetre (Birmingham); **Melford,** David Austin (Cambridge); **Paliwal,** B. D. (Banaras, India); **Paul,** Raymond Wilfred (Cambridge); **Ritchie,** Ronald Hogg (Glasgow); **Ross,** Eric, B.Sc. Met. (Woolwich); **Siddons,** Ronald (Sheffield); **Smith,** Reginald (Moxley); **Staeker,** Richard John (Lidcombe, Australia); **Tate,** Reginald (Sheffield); **Toor,** Amanullah Khan, M.Sc. (Woolwich); **Wallett,** John Keith (Wednesbury); **Wells,** Kenneth Howard (Birmingham); **Williamson,** J. B. P., B.A. (Cambridge); **Wright,** Robert Wilfred Ashby (Birmingham).

The **President** declared the candidates duly elected. They numbered 143, the total membership of the Institute being 4633.

## INDUCTION OF THE PRESIDENT-ELECT

Mr. **Richard Mather,** before vacating the Chair, introduced the new President, Captain H. Leighton Davies, C.B.E. In doing so, he said that there were few men more widely known, both in the Institute and in the industry. Capt. Davies was one of the leading men in South Wales, that very important area in which the industry was carried on with such marked success and enterprise.

Mr. **Richard Mather** then vacated the Chair, which was taken, amid applause, by the new President, **Captain H. Leighton Davies, C.B.E.**

## VOTE OF THANKS TO THE RETIRING PRESIDENT

The **President** (Captain H. Leighton Davies) proposed a vote of thanks to the Retiring President, Mr. Mather, who had been a most congenial and efficient President, and had lived up to the high traditions and efficiency of past Presidents.

The vote of thanks, seconded by Dr. J. W. Jenkin, was carried unanimously, with acclamation, and was briefly acknowledged by Mr. Mather.

## PRESIDENTIAL ADDRESS

The **President** (Captain H. Leighton Davies) then delivered his Presidential Address (*see* pp. 15–37 of the May, 1952, issue of the *Journal*.

## VOTE OF THANKS TO THE PRESIDENT FOR HIS ADDRESS

Sir **Andrew McCance,** F.R.S., (Past-President) moved a vote of thanks to the President for his interesting Address, in which, he said, was concentrated the essence of tinplate knowledge.

The vote of thanks was carried unanimously, with acclamation.

## PRESENTATION OF PAPERS

The following papers were presented and discussed (the dates of publication in the *Journal* are given in parentheses):

*Wednesday, 30th April*

*Afternoon Session*

*Joint discussion on*

"Cold Rolling with Strip Tension. Part I. A New Approximate Method of Calculation and a Comparison with other Methods," by H. Ford, F. Ellis, and D. R. Bland (*May*, 1951).

"Effect of Tension on Torque and Roll Force in Cold Strip Rolling," by W. C. F. Hessenberg and R. B. Sims (*June*, 1951).

"Pressure Distribution between Stock and Rolls in Hot and Cold Flat Rolling," by C. L. Smith, F. H. Scott, and W. Sylwestrowicz (*April*, 1952).

"Softening of Metals During Cold Working," by N. H. Polakowski (*December*, 1951).

*Thursday, 1st May*

*Morning Session*

*Joint discussion on*

"An Experimental Furnace for the Investigation of Open-Hearth Furnace Combustion Problems. Part V—Experiments with the Venturi Port and Modifications Thereof," by J. F. Allen. "Part VI—Summary of Results and their Application in Practice," by J. R. Hall and A. H. Leckie (*January*, 1952).

"Measurement of Air Infiltration in Open-Hearth Furnaces," by R. Haynes (*February*, 1952).

"Aerodynamic Factors Associated with the Wear of Open-Hearth Furnace Roofs," by J. A. Leys and E. T. Leigh (*April*, 1952).

*Afternoon Session*

*Joint discussion on*

"The Determination of Hydrogen in Liquid Steel," by R. M. Cook and J. D. Hobson (*September*, 1951).

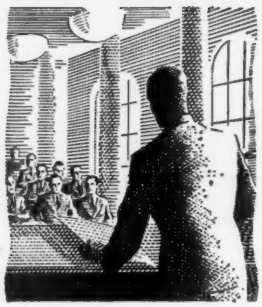
"Diffusion of Hydrogen in Iron and Iron Alloys at Elevated Temperatures," by P. L. Chang and W. D. G. Bennett (*March*, 1952).

"Distribution of Hydrogen in Large Ingots and Forgings," by J. D. Hobson and C. Sykes (*February*, 1952).

"The Effect of Hydrogen on the Properties of Low-Alloy Steels," by J. D. Hobson and C. Sykes (*November*, 1951).

# DISCUSSION ON PAPERS

DISCUSSION AT MEETINGS · WRITTEN CONTRIBUTIONS



## ANNUAL GENERAL MEETING, 1952

THE ANNUAL GENERAL MEETING OF THE IRON AND STEEL INSTITUTE was held on Wednesday and Thursday, 30th April and 1st May, 1952, at the Offices of the Institute, 4 Grosvenor Gardens, London, S.W.1. Mr. RICHARD MATHER, the Retiring President, was in the Chair at the beginning of the Meeting, his place thereafter being taken by Captain H. LEIGHTON DAVIES, C.B.E., the new President.

**Joint Discussion on the Papers—**

### COLD ROLLING WITH STRIP TENSION. Part I—A New Approximate Method of Calculation and a Comparison with other Methods*

*By H. Ford, F. Ellis, and D. R. Bland*

### EFFECT OF TENSION ON TORQUE AND ROLL FORCE IN COLD STRIP ROLLING†

*By W. C. F. Hessenberg and R. B. Sims*

### PRESSURE DISTRIBUTION BETWEEN STOCK AND ROLLS IN HOT AND COLD FLAT ROLLING‡

*By C. L. Smith, F. H. Scott, and W. Sylwestrowicz*

### SOFTENING OF METALS DURING COLD-WORKING§

*By N. H. Polakowski*

Professor **H. Ford** (Imperial College of Science and Technology), who presented the first paper, said that it represented Part I of a report which was in three parts. The other two had been submitted to the Institute but had not yet been published.‖ It was not easy to deal with Part I in isolation, and therefore in his introductory remarks he proposed to make some reference to the two subsequent sections.

Mr. **W. C. F. Hessenberg** (British Iron and Steel Research Association) presented the second paper, Dr. **C. L. Smith** (University of Cambridge) the third, and Mr. N. H. Polakowski (University College, Swansea) the fourth.

Mr. **W. C. F. Hessenberg** (British Iron and Steel Research Association): Mr. Polakowski has tried to explain his interesting results in terms of a mechanical analogy, but such analogies easily lead to absurdities if

* *J. Iron Steel Inst.*, 1951, vol. 168, May, pp. 57–72.
† *Ibid.*, June, pp. 155–164.
‡ *Ibid.*, 1952, vol. 170, April, pp. 347–359.
§ *Ibid.*, 1951, vol. 169, Dec., pp. 337–346.
‖ *See* July, 1952, issue of the *Journal*.

pushed too far. Figure 15 of his paper shows a spring $K$, co-operating with a slider $T$; the force required to move the slider represents the force required to cause the metal to yield—in a copper specimen of cross-section 1 sq. in. this might be 10 tons. Work-hardening is represented by compression of the spring $K$, causing the force required to deform the specimen to rise; in the copper specimen this force may reach 30 tons. On removing the load, the spring, loaded now to 20 tons, would drive the slider back. The copper specimen it represents would certainly not deform itself in the reverse direction when the load was removed.

The model is also qualitatively incorrect. The shape of the real stress/strain curve suggests that the spring $K$ is not linear but gradually weakens, so that each increment of load results in a successively larger increment of displacement. Such a spring would at first imitate the right shape of stress/strain curve, but on reversing the load the new curve would be convex to the strain axis; in fact, as Mr. Polakowski's diagrams show, it is concave to the axis.

Apart from such discrepancies, which can usually be avoided by making the model more complicated, these mechanical analogies do no more than simulate the behaviour of the metal; they add nothing to what is already known. It is now generally accepted that the behaviour of metal can be interpreted satisfactorily only in terms of happenings on the microscopic scale.

Explanations of work-hardening have been given in terms of dislocation theory; it is attributed to the increasing obstruction of the movements of dislocations by various obstacles such as crystal and crystallite boundaries, and to interactions between the dislocations themselves, which increase in number as plastic deformation proceeds. It is plausible to assume that after a certain amount of cold-work a substantial proportion of the dislocations will be thus impeded, and that further increments of external stress will be required to set them moving again. On the other hand, if the external stress system is changed, these obstructed dislocations may be able to move in other directions, thereby evading the obstacles in their original paths. This would result in what Mr. Polakowski has called ' work softening,' and would serve to explain the Bauschinger and similar effects.

It is worth noting that something similar to the Bauschinger effect is observed when a tensile test piece is unloaded after some plastic strain has taken place. On reloading, the metal starts to yield before the stress from which it was unloaded is reached again. It is not unreasonable to assume that the unloading has caused some rearrangement of the dislocation pattern, so that some dislocations which were formerly obstructed have been able, on reloading, to take new paths and travel further before meeting fresh obstructions.

Heat-treatment sometimes results in softening, which has been explained in terms of dislocations diffusing out of the metal so that there are fewer remaining to impede one another; in other cases it causes hardening, which is attributed by the Cottrell theory to the locking of the dislocations by solute atoms that have migrated by diffusion to their neighbourhood. In the former case, cold-work following the heat-treatment will cause hardening as further dislocations are produced; in the latter case, it will first cause softening as the dislocations are progressively torn free from the solute atoms, which are trying to restrain them. The two cases are probably represented by the lower and upper curves of Fig. 14 in Mr. Polakowski's paper.

Dr. **D. V. Wilson** (Department of Industrial Metallurgy, Birmingham University): Mr. Polakowski has shown that the Bauschinger effect and the related ' work-softening ' effects are general properties of cold-worked metals, and that they may be of considerable practical importance. He does not discuss the influence of metallic structure in any detail, however, although it is clear that this will affect the possible magnitude of the effects which he describes.

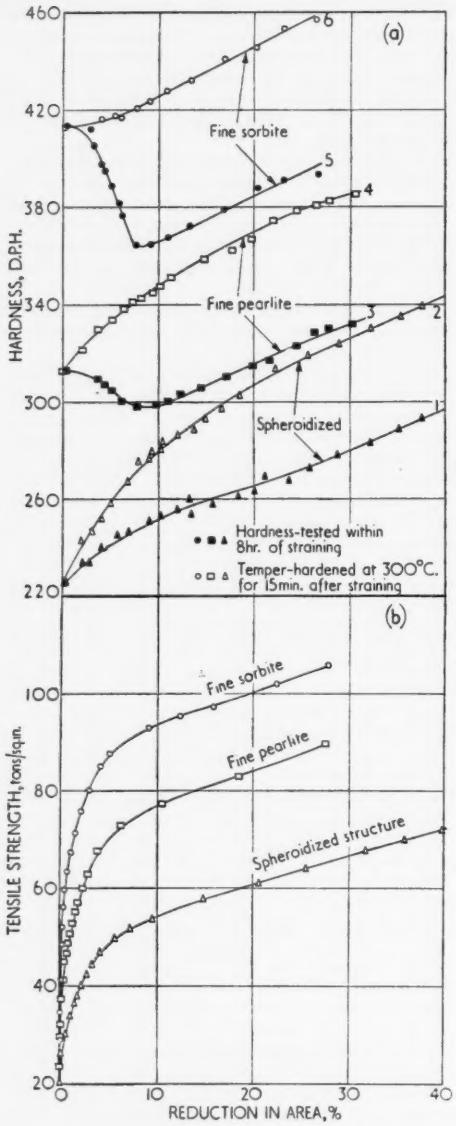
The Bauschinger effect is generally considered to arise as a result of the inhomogeneous character of plastic deformation. The pattern of the plastic inhomogeneities and that of the consequent internal stress system may vary very widely, both in scale and intensity, with the material and with the method of working. I would like to discuss some of the effects of microstructure in the case of steel specimens which have been subjected to deformation that is essentially homogeneous on a macroscopic scale.

In polyphase alloys such as steel, the hard particles of the secondary phase may provide effective local barriers to the process of slip in the matrix. It is clear that a system of textural stresses will develop, between the hard particles and the relatively soft matrix, as a result of plastic deformation. The level which such microscopic internal stresses may reach is less clear, since this will depend on the properties of the particles themselves and of the interface between the particles and the matrix, and also on the extent to which yielding of the matrix may be constrained in the neighbourhood of the particles.

Some experiments which I have made on steel suggest that, as one might expect, the smaller the carbide particle size in a given steel the more intense are the locked-up stresses which the material may sustain. Moreover, in cold-worked steels of fine microstructure the residual strains in the cementite particles may reach very high values, probably in excess of 1% mean strain.[1] It is not surprising, therefore, that a larger Bauschinger effect is obtained with medium- and high-carbon steels than with low-carbon steels or with one-phase alloys. Indeed, the conditions in which Mr. Polakowski has usually examined his steels—that is, the fully annealed and spheroidized conditions—are those which will minimize the difference between the steels and the (effectively) single-phase materials. If we carry out reversed straining experiments on a hard-drawn, high-carbon steel wire having a fine pearlitic microstructure, the observed reduction in indentation hardness may exceed 60 D.P.H.

Using a high-carbon steel, it is possible to obtain X-ray diffraction evidence of the balanced residual stress system which is set up between the cementite particles and the ferrite during cold-working, as a result of their differing plastic properties.[2] These microscopic internal strains are, of course, orientated with respect to the direction of working. It is interesting to find that (so far as may be judged from the X-ray results) when a cold-worked specimen is subjected to reversed straining, the minimum indentation hardness occurs after a degree of reversed straining which is of the same order of magnitude as that required to eliminate the directional component of this interphase stress system. Also, in contrast to the behaviour of long-range or ' body ' stresses, quite large reversed plastic strains (10–20% reduction) appear to be required to eliminate the directional short-range textural stresses. I think that this must be explained in terms of a dislocation picture, as Mr. Hessenberg has suggested. One can imagine that a build-up of dislocations of like sign occurs at some form of barrier to plastic flow.

Incidentally, on reheating a cold-worked high-carbon steel, the interphase textural stresses are not fully elaxed until the steel reaches temperatures significantly higher than 400° C. One would not expect, therefore, that Bauschinger effects arising from this cause would




Heat-treatments preceding straining:
Curves 1, 2 Spheroidized at 680° C. for 8 hr.
3, 4 Transformed in a salt bath at 470° C. (microstructure principally fine pearlite)
5, 6 Quenched at 200° C., cooled to room temperature, and tempered at 300° C. (microstructure principally fine sorbite)

**Fig. A—Properties of a steel containing 0·74% C, 0·36% Mn, 0·09% Si, 0·01% S, and 0·03% P, in three different metallurgical conditions : (*a*) Influence of tensile straining on indentation hardness ; (*b*) true tensile-stress/strain relationships**

be eliminated by low-temperature reheating, as Mr. Polakowski has demonstrated.

I am interested in the ' work-softening ' effects shown by sorbitic steels, to which Mr. Polakowski refers. In such materials a reduction in indentation hardness occurs, as a result of moderate degrees of plastic deformation, without the necessity of prior cold-working. Apparently this effect is associated with the reorganization of an existing textural stress system in a duplex structure. In a heat-treated steel the stress fields associated with the individual particles of carbide will add up to provide an effectively isotropic hardening of the material as a whole. On cold-working, a directional pattern of textural stresses will replace this initial stress system, and yield strength will become a directional property; that is, the yield strength will increase progressively in the direction of working, but, so far as the influence of the textural stress system is concerned, the yield strength of the material in directions perpendicular to the direction of working may at first decrease.

Practical results suggest that if the initial textural stresses are of a sufficient magnitude, and if other factors are favourable, the average hardness of the material may at first decrease on cold-working. Figure *A* (*a*) shows the influence of tensile straining on the indentation hardness of a 0·7% C steel in three different conditions of initial hardness and microstructure. It illustrates the important influence which the microstructure has on the extent of the ' work-softening ' effect. Hardness tests were carried out immediately after straining (*see* curves 1, 3, and 5). The spheroidized material did not show the softening effect, the intermediate hardness material showed a small effect, and the fine sorbitic material showed a very large one. I took great care to avoid artificially ageing these materials after straining, because in practice the hardness increments obtained on ageing are fairly large. Curves 2, 4, and 6 show the effect of reheating the strained specimens at 300° C. for 15 min.; the temper hardening is considerable. These curves illustrate one of the dangers of taking hardness as a criterion of internal strain energy. Probably the internal strain energy decreases in strain-age hardening and in temper hardening. It is also interesting that a material which shows a large work-softening effect shows a large temper-hardening increment ; before we can reach a full explanation of these phenomena, we may have to take into account the influence of the carbon atoms in the ferrite matrix, as Mr. Hessenberg has indicated.

However, there is no doubt that the effects of the microscopic textural stress system are very important. Figure *A* (*b*) shows the ' true ' tensile-stress/strain relationships of the same three specimens referred to in Fig. *A* (*a*). There is nothing unusual about these relationships. The

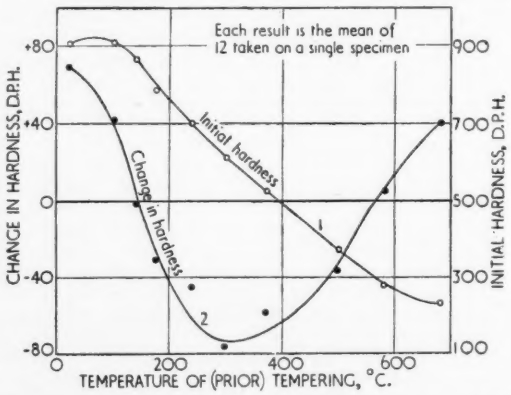



**Fig. B—Influence of previous heat-treatment on the change in indentation hardness, due to 10–15% reduction by compression, of a steel containing 0·88% C, 0·26% Mn, 0·04% Si, 0·01% S, and 0·03% P. (The first three values for curve 2 may be slightly low, because of local cracking in compression)**

tensile stress increases progressively from the start of straining, and in fact there is an indication that the work-hardening, as judged from the changes in tensile stress, increases as the microstructure becomes finer. Figure *A* illustrates a most important point: that these work-softening effects are directional. Unless one appreciates the directional nature of these effects, one may be led to erroneous conclusions about changes in the resistance to deformation.

We may conclude that the extent of the work-softening effect may be influenced by the intensity and directional characteristics of the initial textural stress system. However, the scale of the internal stress pattern may also be important. Using compressive straining, the influence of a very wide range of initial structures can be studied. Figure *B*, which refers to results obtained with hardened and tempered specimens of a 0·88% C steel, is of interest in this connection. All the specimens were water-quenched from 800° C., immediately cooled in liquid oxygen, and then tempered for 2 hr. at the temperature shown, before straining. The initial hardnesses after the tempering treatment are given in curve 1. The specimens were strained within the range 10–15% reduction, which gives about the maximum degree of work-softening, if this occurs. Up to an initial hardness of about 600 D.P.H., the degree of work-softening increased with the hardness until the reduction in hardness reached a value approaching 80 D.P.H.; but beyond 600 D.P.H. the observed softening was less, and martensite tempered below 140° C. did not show the work-softening effect, although the initial internal strain energy would have continued to increase with hardness.

This pattern of behaviour is exhibited by a variety of steels. As Mr. Polakowski has already shown, the effect is sensitive to the carbon content, steels near eutectoid composition showing a large work-softening effect. Alloy steels generally show a smaller effect than equivalent plain carbon steels.

If the behaviour of hard steels is strongly influenced by the scale of the structural inhomogeneities that are present, then the same general pattern of behaviour will be shown by quite different alloys which have analogous structural features. I have made a few experiments with Duralumin, using tensile straining; the results are given in Fig. *C*. Before straining, all the specimens were water-quenched from 495° C., aged at room temperature for eight months, and then aged at the stated temperatures for 10 hr., followed by slow furnace cooling. The results suggest that, in this case also, the lowest initial work-hardening, as judged by the indentation hardness test, is obtained with material in which very small separate particles of the second phase are present.

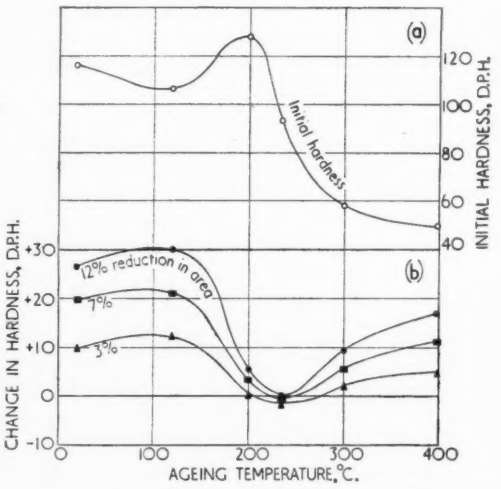



**Fig. C—Influence of previous heat-treatment on the change in indentation hardness, due to tensile straining, of duralumin (3·9% Cu, 0·96% Mg, 0·35% Si, 0·40% Mn, 0·51% Fe, 0·07% Ni). (*a*) Initial hardness; (*b*) change in hardness**

I suggest that a possible explanation of these scale effects may be visualized in terms of the theories advanced by Mott and Nabarro,[3] and by Orowan,[4] relating to the influence of the scale of the internal stress pattern, in solid solutions and duplex alloys, on the movement of dislocations. In brief, they consider the forces required to bend the dislocation line to a given radius, and conclude that the spacing of solute atoms in a solid solution will generally be too close to allow a dislocation to bend, during plastic flow, around the regions of high internal 'stress' that are associated with individual solute atoms. In a two-phase alloy, on the other hand, even in the early stages of precipitation the distances between the particles of the precipitate may be sufficient to allow the formation of dislocation loops around the individual structural inhomogeneities.

If the mechanism of plastic flow in an alloy containing a fine precipitate is such as to allow a build-up of dislocations to be associated with individual particles of the precipitate, for example by the formation of dislocation loops around each particle, then the initial textural stress system associated with the precipitate may be changed completely as a result of plastic deformation. In these circumstances, I suggest, indentation hardness tests may indicate abnormally low rates of work-hardening during the early stages of deformation.

Professor **H. O'Neill** (University College, Swansea): Referring to Mr. Polakowski's paper, one interesting point about the phenomenon that a cold-worked metal can be softened by more cold-work is the effect which it may have upon the mechanics of hardness testing itself, because the usual indentation procedures naturally apply further cold-work to the metal. If the specimen to be tested is already cold-worked, then the actual indentation operation may produce some work-softening within the specimen. The hardness test has always been complicated, but this new feature may be a little disturbing.

On p. 344 the author states, "Incidentally, for equal linear deformation, extension causes more work-hardening than compression both in steels and in cubic non-ferrous metals." There are directional effects in cold-working that may produce work-softening, and the difference referred to between the effect of compression and that of tension may well be connected with the hardness test, so that the application of methods of strainless indentation will probably have to be considered.

If it is confirmed that cold-working under certain conditions produces work-softening, it may similarly produce a lowering of the fatigue value. The significance of Meyer hardness analysis may also have to be reconsidered. For example, in cold-working a stage is sometimes reached, early in the progressive deformation, at which the Meyer $n$ value reaches its lower limit of 2·0, indicating that the metal cannot be further strain-hardened. Copper reaches this limiting $n$ value at about 25% reduction, and yet will still continue to work-harden. The reason for this has never been understood, but work-softening may have some effect.

Professor **H. Ford** (Imperial College of Science and Technology): In the paper by Hessenberg and Sims is given the first comprehensive set of experimental results of tension rolling tests to be published. In view of the expense of carrying out such tests, and the organization and background of experimental knowledge which are required, I think it is unlikely that further information of this sort will be forthcoming from any other source, either here or abroad, for some years. It is a pity, therefore, that more space in the paper has not been given to the experimental results, as compared with the theoretical speculations, and that other metals, notably copper, have not been used in the tests. The information given in Table II, for example, is not sufficient for use by other workers who may wish to check their own ideas or make comparisons with their own experimental results; the thickness of the strip into and out of each pass is not given, but the nominal values are useless for reliable comparisons.

The usefulness of equations (3) and (10) depends on how accurately the values of $P_0$ and $G_0$ (the roll force and roll torque with zero tensions) can be read from the graphs, and it is difficult, therefore, to check the value of the computational method put forward by the authors. In particular, in Table II for Coil 2 (the last line but one of the experimental results) an experimental roll-torque value of 1·14 tons-in. per inch width is clearly out of relation with the values on each side of it; yet the author's computational method seems to deal with this happily and gives good agreement with an obviously erroneous experimental value. Using the author's method and taking the best possible value of $G_0$ (no tension torque), $G$—the torque with tension—for that particular pass is 0·045 ton-in., giving an error of several hundred per cent. I then recalculated the values of $G_0$ and $P_0$ from their equations (3) and (10) and the values of $G$ and $P$ given in Table II, and I find that the agreement with the values as judged from Figs. 2 and 3 is not very good.

It would appear that equation (3) should include the quantity $(1 + f)$, where $f$ is the forward slip, since equation (3) is derived from equation (2). If this factor is included and $G$ is recalculated, there is a bigger scatter of the results than is indicated in Table II, and the agreement is particularly bad for high tensions.

Although the roll force equation (10) is derived from theoretical considerations, it cannot be used unless $P_0$ is accurately known (presumably either from a rolling test or from one of the theories of rolling). It would seem from the Tables that values of $P$ (the roll force with strip tension applied) can be up to 20% in error, so that if, as I believe, the present state of knowledge allows us to calculate $P_0$ only to $\pm$ 10%, the overall inaccuracy may be $\pm$ 30%. On the other hand, if $P_0$ and $G_0$ are determined from an experimental rolling test, why not apply the appropriate tensions to the strip directly and measure the values of $P$ and $G$ in the mill itself?

Equation (3) is perhaps more accurate than equation (10), but on the other hand, methods of computing $G_0$ are less accurate at present than those for calculating $P_0$, and about the same overall error exists.

The authors claim that their method has distinct advantages over other methods for purposes of practical calculation. Although equations (3) and (10) certainly involve only simple calculations, it is doubtful whether the saving in time compensates for the loss of accuracy: a more accurate method may save time in many cases.

Reference has been made to the error introduced by the equation of Bland and Ford for the case where high back tension is applied to the strip. This error is serious only where the strip is soft, and in practice it is unusual to apply a high back tension to the first pass on hot rolled band.

Mr. **R. B. Sims** (British Iron and Steel Research Association): The authors of the first paper have pointed out that passes rolled with tensions provide a searching test for any theory of rolling. On p. 67 they draw attention to a discrepancy between the roll forces and torques obtained from the pressure distributions calculated from Orowan's equations, the original equations of Bland and Ford, and the present approximate method. The reason for these discrepancies has been mentioned in the paper by Hessenberg and Sims. It can be shown that the distribution of roll pressure calculated from Orowan's 'general' method may be rewritten in the form:

$$s^+ = s_0^+ - \sigma_2 \exp[\mu\psi(\phi)]$$
$$s^- = s_0^- - \sigma_1 \exp\mu[\psi(\phi_1) - \psi(\phi)]$$

where, in the authors' notation,

$$\psi(\phi) = \frac{2\left(1 - \frac{h_2}{2R'}\right)}{\frac{h_2}{2R'}\left(2 + \frac{h_2}{2R'}\right)} \tan^{-1}\left[\sqrt{\frac{2 + \frac{h_2}{2R'}}{\frac{h_2}{2R'}}} \tan\frac{\phi}{2}\right] - \phi$$

When $h_2/R'$ is small, as is always the case in cold strip rolling,

$$\psi(\phi) \to \frac{R'}{h_2}\tan^{-1}\sqrt{\frac{R'}{h_2}}\cdot\phi - \phi$$

Hence:

$$s^+ = s_0^+ - \sigma_2 \exp\left[\mu\{H - \phi\}\right]$$
$$s^- = s_0^- - \sigma_1 \exp\left[\mu\{H_1 - H\} - \mu\{\phi_1 - \phi\}\right]$$

and to a first approximation these equations become:

$$s^+ = s_0^+ - \sigma_2 \exp[\mu H]$$
$$s^- = s_0^- - \sigma_1 \exp\left[\mu\{H_1 - H\}\right]$$

Bland and Ford's equations are:

$$s^+ = s_0^+ - \frac{kh}{k_2 h_2}\sigma_2 \exp[\mu H]$$

$$s^- = s_0^- - \frac{kh}{k_1 h_1}\sigma_1 \exp\left[\mu\{H_1 - H\}\right]$$

The discrepancy, therefore, is in the factors $kh/k_1h_1$ and $kh/k_2h_2$ of the tension component of the roll pressure in Bland and Ford's equations.

For forward tension, $kh \simeq k_2h_2$, and hence the error with applied front tension is small; but for drag tension on annealed stock, $kh \gg k_1h_1$ and the error in roll pressure may be considerable, as the authors have found. This discrepancy will be smaller when a mean yield stress is used, for then

$$s^- = s_0^- - \frac{h}{h_1}\sigma_1 \exp\left[\mu\{H_1 - H\}\right]$$

and the theory will tend to underestimate the effect of tension in comparison with Orowan's equation, as is seen from Table I on p. 66 of their paper.

It seems logical to rewrite Bland and Ford's original equation in the form:

$$s^+ = \left(\frac{kh}{h_2} - \sigma_2\right)\exp[\mu H]$$

$$s^- = \left(\frac{kh}{h_1} - \sigma_1\right)\exp\left[\mu\{H_1 - H\}\right]$$

and a proof of the validity of these equations will be published later by Bland and myself.

Although this method will be of great interest to students of rolling technology, it possesses a major dis-

advantage from the viewpoint of the busy mill engineer, in that the value of the deformed roll radius must be calculated by a series of approximations. In the examples chosen by Ford, Ellis, and Bland, the approximation to $R'$ converges rapidly, but in many instances when rolling wide thin strip it will be found that, for the combination of yield strength, roll diameter, and strip thickness, $R'$ converges very slowly and sometimes fails to converge at all. Considerable time and patience is often required, therefore, in completing the calculation.

Many mill engineers would gladly exchange a small percentage of accuracy for time saved in calculation, particularly as the calculation of the effect of applied tensions assumes major importance only in specifying reel and main mill motors. There is much to recommend equations of the form:

$$P = P_0 f_P(\sigma_1 ; \sigma_2)$$
$$G = G_0 f_G(\sigma_1 ; \sigma_2).$$

The value of $P_0$ may be calculated without approximations from values of $R/H$ (not $R'/H$), $k$, and $r$, and a solution in this form has been obtained and will be presented shortly.

Having obtained an accurate value of $P_0$, the effect of tensions could then be obtained from a simple factor involving tensions only. With this in mind, Hessenberg and Sims have suggested the use of the equations

$$P = P_0\left\{1 - \frac{\sigma_1 + \sigma_2}{2\bar{k}}\right\}$$
$$G = G_0 - \tfrac{1}{2}Rh\{\sigma_2 - \sigma_1\}.$$

The torque equation, based on the assumption of constant energy, is reasonably accurate. The roll force equation has been much criticized, since it gives equal weight to both front and back tension. This equation can easily be modified, and it will be shown, in a proof to be published separately, that

$$P = P_0\left\{1 - \left[\frac{\frac{\phi_n}{\phi_1}\sigma_2 + 1 - \frac{\phi n}{\phi_1}\cdot\frac{\sigma_1}{(1-r)}}{\bar{k}}\right]\right\}$$

The ratio neutral-angle/entry-angle may be presented in tabular form as:

$$\frac{\phi_n}{\phi_1} = \text{function}\left[\mu\sqrt{\frac{R'}{h_2}} \; ; r \; ; \; \frac{1 - \frac{\sigma_1}{(1-r)k_2}}{1 - \frac{\sigma_2}{k_2}}\right]$$

Except at very high back tensions at high reductions, this equation gives values of roll force within a few per cent. of values calculated from Orowan's equations.

I would venture to suggest, however, that the mill engineer will prefer to use Hessenberg and Sims's equations, despite the fact that they may give inaccuracies of as much as 10%.

In regard to the third paper, Smith, Scott, and Sylwestrowicz are to be congratulated on carrying out one of the most difficult pieces of experimentation in the whole field of rolling research. In any measurement of roll pressure, the measuring instrument itself must be subjected to the heavy stresses of the roll gap, and must be robustly constructed while possessing great sensitivity and rapidity of response. The glass-block dynamometer used in the experiments has many of these attributes, particularly in speed of response, although it possesses the added complexity of an optical train, which needs very careful adjustment. The principal objection to the experimental arrangement, and one for which I see no practical alternative, is in the use of a pin in the roll surface. The authors state on p. 351 that the pin assembly was built with an elasticity (which I presume

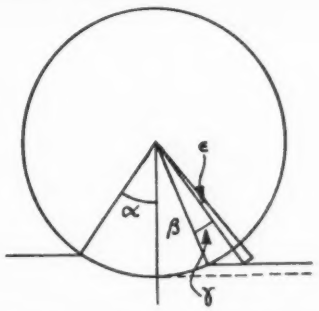



**Fig. D—Diagram showing corrections for pin projection**

is the elastic modulus $M$ of the equipment) nearly equal to that of the roll. Unless the coincidence was very close, the pin may have protruded through the roll on loading ($M_{roll} < M_{pin}$) or may have been pushed into the roll by the material ($M_{roll} > M_{pin}$). If the effect were considerable, the data given in Fig. 8 imply that the load error may be large. The impression left by the pin on the strip would only represent the projection of the pin at the end of the arc of contact, because the impression made before the rolls and strip separate would have been removed by subsequent rolling—in this respect the pin behaves like the scratch made in the rolls, for measuring forward slip.

There are two corrections to their results which are not mentioned by the authors. These are $\gamma$, due to the projection of the pin, and $\beta$, arising from the fact that the leading edge of the pin makes contact first with the strip, and the trailing edge is last to leave it. In angular measure, the angles shown in Fig. *D* are:

$\alpha = \sqrt{\delta/R'}$, where $\delta$ is the plastic reduction
$\beta = \sqrt{eh/R'}$, where $e$ is the elastic strain of recovery and $h$ is the final thickness of the strip
$\gamma = \sqrt{2b/R}$, where $b$ is the projection of the pin
$\epsilon = a/R$, where $a$ is the diameter of the pin.

If the pin protrudes before rolling as the roll deforms under the load applied just ahead of the pin, an additional correction of the same order as $\gamma$ would be required.

In the example quoted by the authors (Fig. 12*c*):

$H = 0{\cdot}2$ cm.; $h = 0{\cdot}118$ cm.; $\delta = 0{\cdot}082$ cm.
$R' \simeq 8{\cdot}65$ cm.

Thus:

$$\alpha = \sqrt{\frac{0{\cdot}082}{8{\cdot}65}} = 0{\cdot}0974 \text{ rad.} = 5{\cdot}69°$$

$$\beta = \sqrt{\frac{0{\cdot}0025 \times 0{\cdot}118}{8{\cdot}65}} = 0{\cdot}0172 \text{ rad.} = 0{\cdot}97°$$

$$\gamma = \sqrt{\frac{2 \times 0{\cdot}001}{8}} = 0{\cdot}0125 \text{ rad.} = 0{\cdot}72°$$

$$\epsilon = \frac{0{\cdot}07}{8} = 0{\cdot}009 \text{ rad.} = 0{\cdot}52°$$

and therefore the total angle $(\alpha + \beta + \gamma + \varepsilon) = 7{\cdot}90°$.

The authors obtain a trace of approximately 9° in this experiment, 3° of which they attribute to elastic recovery. Could they please indicate the error of these calculations, or alternatively indicate the reason for their longer arc of contact?

They have also found that at reductions over 20% on their material, which had a width/thickness ratio of 20, there was a falling-off of roll pressure as the edge of the strip was approached. They do not assess the difference between the actual roll force found and the roll force assuming plane deformation, although from Fig. 16 the effect would appear to be considerable.

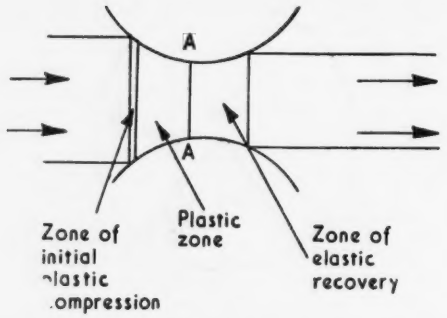



**Fig. E—Diagram of roll gap**

Experiments have been carried out, in the Rolling Mill Laboratory, in which strips of steel 0·1 in. thick and 0·5–5 in. wide, all from the same coil, were rolled to reductions between 5 and 50% in one pass. The maximum variation of roll force was ± 3%, and the specific roll force for the 5-in. and ½-in. wide materials was slightly greater than that for the 2-in. wide stock. The variation is well within possible experimental error due to inaccuracies in the roll-force meters and known variations in lubricating conditions; hence it may be said that in these experiments no variation of specific roll force with width was found for width/thickness ratios between 5 and 50.

Mr. **M. F. Dowding** (Davy and United Engineering Co., Ltd.): To compare the two papers dealing with the effect of strip tension is perhaps invidious, but from a mill builder's point of view the method which produces the answer more quickly, even if it does sacrifice a little accuracy, is the more useful. The method described by Hessenberg and Sims has certainly proved useful to us, but it presupposes that $P_0$ and $G_0$ can be readily computed. These values can be obtained from the nomograms put forward as a graphical solution in a previous paper by the same authors.[5]

At first sight, the theoretical proof that both back and front tension reduce rolling load seems to be a welcome advantage to the mechanical designer, because if he finds that a pass is going to overload either the roll necks or their bearings, he can apply tension and reduce the load to bring it within the available capacity. However, in practice—and this should be confirmed by the strip rollers—there are times when other considerations preclude the use of front and back tension, and this applies particularly to a high-speed mill.

In designing his schedule, the rolling-mill manager likes to use heavy tension when the metal is thick and still ductile. For example, when rolling, say, tinplate on a roughing mill it is possible to apply a fairly heavy tension front and back in the early passes, but by the last pass, when the metal is hard and the reduction is about 35%, front tension should not be more than is needed to keep the coil from collapsing, and even back tension has little effect on the mill load.

Hessenberg and Sims state that once the function $R/h$ exceeds 150, their calculations are inaccurate. In practice, the last pass of a tinplate mill is taken with a roll radius of 10 in. and a strip thickness of 0·013 in., which gives an $R/h$ value of 770; it is clear, therefore, that practical considerations must not be overlooked when we are designing a theoretical pass schedule.

Mr. **D. R. Bland** (Imperial College of Science and Technology): Part III of our paper[6] deals with the calculation of the contribution to the roll force from the elastic part of the roll gap. In Fig. *E*, a diagram of the roll gap, the minimum thickness is at $AA$, and the strip recovers before it leaves the roll gap. We have calculated the contribution to the roll force from this part of the roll surface, and find that in many cases it reaches 15%; the average figure is 7–8%. In the course of this calculation we were able to derive the total length of the arc of contact where the strip was in an elastic condition, and therefore also the angle at the centre. The latter can also be obtained very quickly by rough calculation, and the result disagrees with that ascertained by Smith, Scott, and Sylwestrowicz in their measurements.

The well-known formula for the angle subtended by the elastic part of the arc of contact is $\sqrt{\delta_e/R'}$; $\delta_e$ is the change of thickness of strip due to elastic compression, and is approximately $k/E \times h_2$, where $h_2$ is the final thickness, $k$ is the yield stress, and $E$ is Young's modulus. Thus the angle is $\sqrt{h_2/200R'}$, *i.e.*, about $\frac{1}{200}$ rad. or approx. $\frac{1}{3}°$. This contradicts the result of Smith and his co-authors, who give about 2° for the length of the subtended part of the arc of contact.

Mr. **N. H. Polakowski** (University College, Swansea): The three interrelated papers on cold rolling offer an opportunity for comparing some aspects of the mathematical theories of rolling put forward in recent years with the experimental results obtained either in works or during laboratory tests. In this connection the paper by Hessenberg and Sims is particularly valuable, since it offers a realistic basis for discussion. The circumstance that the rolling results reported by these authors were obtained at speeds much below those used commercially does not detract from the value of the work, although a few comparative tests at rolling speeds of, say, 200–300 ft./min. would have been welcome.

The salient feature of their results is the remarkable constancy of the energy-consumption figures for any given percentage draft, irrespective of the combination of tensions used. Equation (3) is legitimately based upon this observation; however, with coil 3, for example, there is a small but systematic fall in the energy values as the tension in the strip increases. This effect can be seen in the third group of results for coil 5, and perhaps in the last group of results for coil 6. Similar effects are observed between the various groups of results.

On p. 163 the authors suggest that this fall of energy values is connected with the decrease of frictional losses as a result of the heavy pulls in the strip. They also say that their torque equation should be used with caution when thin strip is rolled between large rolls. I do not think that this is necessarily so, at least with steel; in my opinion, their energy consumption differences can be satisfactorily accounted for by simple metallurgical factors, without reference to the possible dependence of the frictional losses on tension. A closer scrutiny of the figures in the individual groups indicates that whenever the decrease of energy caused by an increase of tension exceeds 5–6%, the drafts are also lighter. In coil 5, for example, with only 12 tons/sq. in. back pull and zero front tension, the energy consumption is 20·3 h.p.hr./ton, but with 12 tons/sq. in. back and 20 tons/sq. in. front pull, the energy figure is only 17·3 h.p.hr./ton, a difference of 15%. At the same time, however, the draft is also 9% less, so that the net difference of energy is only 6%. The explanation may well be that deformation in tension rolling is accomplished by a combination of compression and tension; the tensile contribution increases as the tension per square inch is increased. In steel, the tensile yield stress is always less, for equal reduction, than that in compression,[7] and the difference between the appropriate yield-stress curves is of the right order to account for the reported differences of energy consumption. In addition, since the initial yield points of annealed steel

in tension and compression are equal, it is only natural to expect the effect of tension on deformation energy to be greater on pre-rolled material.

Kenyon[8] has published much information on energy consumptions per ton of reduced steel strip, obtained on a variety of large single-stand and tandem mills with 16–21 in. dia. rolls, rolling both sheet and tinplate gauges. His values were computed from ordinary meter readings, and thus include all possible losses; nevertheless, they agree fairly well with those obtained by the present authors on their comparatively small mill. Recent Russian results[9] refer to rolling soft steel strip on a small three-stand tandem mill with 2·5-in. dia. rolls, at alternative rolling speeds of 130 and 2800 ft./min., but only to 60% overall reduction. These results again indicate that the energy per ton rolled does not depend on speed. The constancy of energy consumption for any given reduction, irrespective of rolling conditions, is also confirmed by Dahlstrom.[10]

The authors' statement that rolling with back tension is actually less efficient than rolling without it obviously applies only to single-stand mills with drag generators or friction brakes. In tandem mills and some single-stand equipment which I have recently described elsewhere,[11] the tension work is completely recoverable.

Perhaps Professor Ford and his colleagues would comment on this remarkable constancy of deformation energy for a given reduction—it seems to me that this fact controverts not only their constant friction assumption but also the very foundations of their theories.

I would also like to draw attention to an important limitation of Hitchcock's equation, which is so often used. As an elementary derivative of Hertz's formula for elastic contact between two parallel elastic cylinders, it must necessarily involve the same assumptions. The important one is that there is no friction between the contacting bodies, and that consequently the resultant of all forces normal to the roll face passes through the axis of the roll. In fact, precisely the opposite happens, and this leads to several fairly obvious conclusions. Can anyone suggest what shape the roll face is actually likely to assume under the combined action of normal and tangential stresses, and how to determine this shape analytically?

With reference to the paper by Smith, Scott, and Sylwestrowicz, it is a pity that the experiments have not been extended to wider strips. If this were done, they might obtain confirmation or otherwise of an effect shown in Fig. *F*.[12] This shows that the pressure distribution across a narrow strip is similar to that obtained by Siebel and Lueg[13] in 1933, and also by Smith and his co-workers, but that the pressure becomes uniform as soon as the width/thickness ratio exceeds 20; the general belief that the pressure across a wide strip is uniform thus seems to be correct.

Dr. **B. B. Hundy** (British Iron and Steel Research Association, Sheffield): The results in Mr. Polakowski's paper agree with some of my work on the softening of copper during cold rolling. Copper strip was given a reduction of 6% in two passes, keeping the direction of rolling the same for each pass; microhardness measurements showed a surface hardness of about 77 and a core hardness of 70. Another sample of the same material was then given the same reduction, but this time the strip was reversed end to end before the second pass. The core hardness was substantially the same as before, but the surface hardness was only 71. It seems that reversal rolling gives a product with a lower surface hardness than does straight rolling.

During some other work, I found that Armco iron torsion specimens fractured at a surface shear strain of 3·5 when twisted in one direction only. The same material, however, could be twisted to a strain of 2·5 and then untwisted before fracture occurred, giving a total strain of 5 compared with 3·5.

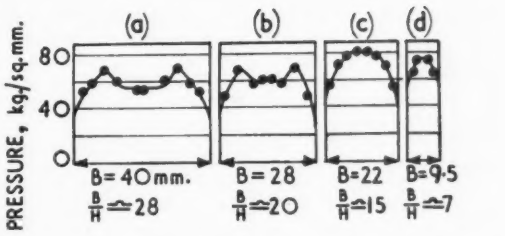



**Fig. F—Pressure distribution across bronze strips of varying width *B*. Initial thickness $H = 1{\cdot}4$ mm.; draft = 22%. (By courtesy of Mr. H. Brutcher, California, U.S.A.)**

I agree with Dr. Wilson's remarks on the effect of microstructure on this phenomenon. Silver steel was treated to give specimens in the spheroidized and normalized conditions, which were prestrained about 5% in tension. Samples cut from these were compressed various amounts, and the hardness of each sample was measured. The hardness fell from 336 to 302 in the pearlitic steel and from 222 to 203 in the spheroidized steel. The minimum hardness occurred at a compressive strain of 9% in the pearlitic and at 5% in the spheroidized steel. I think that greater microstresses are to be expected in the steel with the pearlitic structure, and it seems that these results support the explanation of this phenomenon based on residual stresses. The results, however, might also be explained on Mr. Hessenberg's theory of dislocations, which depends upon the free path along which dislocations can travel. In the pearlitic steel the path will be shorter, in some directions, than in the spheroidized steel, but the free path may be quite long if the dislocations travel along the lamellar plates.

In these experiments it was found that the magnitude of the softening depends upon the direction of the hardness testing. The values I have mentioned were obtained from tests on the ends of the compression specimens; when we filed flats on the sides of the specimens and carried out hardness tests there, the magnitude of the effect was reduced considerably, to a value of approximately 6 points instead of 20 or 30.

## CORRESPONDENCE

Mr. **A. Allison** (Sheffield) wrote: Mr. Polakowski has studied a phenomenon of some importance in deep pressing and cold-working, particularly in connection with reverse drawing operations. That the temperature of recrystallization usually decreases with increasing amounts of cold-work, and that reversal of the direction of straining produces an increase of recrystallization temperatures, is only to be expected, in view of the essential microstructure.

He suggests that the softening produced by compression after tension may be due to the breakdown of a system of internal stresses and to decrease of latent or internal energy. I would like to suggest that this internal stress system or latent energy might be expressed in another way.

In cold-working, the deformation produced by slip on the cleavage planes is indicated by lines, visible under the microscope, which are of amorphous or martensitic material. Such material possesses latent energy in the sense that it is metastable and easily recrystallized on heating.

I have previously quoted an example[14] of a lightly cold-worked bar that had been reverse-cold-worked by 'up-ending' in a simple pressing operation. In that example there had been complete recrystallization, which, in my opinion, could only be due to internal heat produced momentarily during the operation of 'up-ending.' Russell's[15] calculated values of the potential energy of cold-working seem to confirm this view.

Dr. Polakowski's test pieces might yield information under microscopic study, as I think the softening recorded could not have been produced without a considerable measure of recrystallization of the amorphous or martensitic material produced in the first straining.

His views on latent energy correspond with the above and also with the 'germinative' temperature of critically strained mild steel when annealed. That is, a mild steel given a critical amount of strain and annealed at a critical temperature possesses an unusual capacity for forming very large crystals, and this capacity may be described as latent energy.

## AUTHORS' REPLIES

Professor **Ford** wrote in reply: Mr. Sims has commented on the discrepancy, for passes on annealed strip with high back tension, between the values of roll force and torque obtained from the pressure distribution calculated from Orowan's equations and the original equations of Bland and Ford. One of us (D. R. Bland) is associated with Mr. Sims in a paper (to be published elsewhere) dealing with this discrepancy, but we are grateful to Mr. Sims for quoting the main conclusions to be drawn from that paper. We would, however, point out that in the original paper the approximation was clearly stated, and this approximation allowed the simplified equations, upon which the equations given by Mr. Sims are based, to be derived. These equations as amended now give a very close approximation to the more exact solution due to Orowan, while allowing calculations to be carried out much more easily than is possible with Orowan's method. We would, however, like to point out that:

(*a*) First passes on annealed strip are not, in practice, carried out with high back tension, and accordingly the case is not of much practical importance.

(*b*) The comparisons to which Mr. Sims refers are between calculation methods using the stress/strain curve applicable to the work-hardening in the roll gap. The comments are not, therefore, really relevant to the method put forward in the present paper, in which a constant mean yield stress over the arc of contact is used; as Mr. Sims himself remarks, the errors between the calculations are not then important.

(*c*) If a comparison is made between the theories and experiment, there appears to be no particular advantage in Orowan's method as compared with the present approximate method. This can be seen from Part II[16] of the present series of papers.

Mr. Sims also remarks on the convergence of $R'$ in these calculations. We are surprised that he considers that in some cases the calculations fail to converge at all. We cannot understand how this can happen, and over the very large number of calculations we have carried out we have found it seldom necessary to repeat the calculation more than once. When the method was first put forward[17] we also pointed out that it was only necessary to calculate two values of roll force with appropriate values of the radius $R'$, the correct value for the consistency of $R'$ and $P$ being obtained by a simple interpolation. It is therefore unnecessary to rely on successive guesses at the values, as suggested by Mr. Sims. We would also refer to equation (69) on p. 162 of the paper referred to, which allows a first approximate value of roll force to be obtained.

Both Mr. Sims and Mr. Dowding have commented on the practical use of these calculation methods. Both state that the rolling-mill designer would gladly exchange a small loss of accuracy for time saved in the calculation. We would, of course, agree with them if it was a question of a small loss of accuracy, but (as pointed out previously in this discussion) the possible errors arising in the method of Hessenberg and Sims must be taken in conjunction with the errors involved in the initial calculation of $P_0$ and $G_0$. From the tests we have made with this method, we estimate that the overall accuracy is not much better than $\pm$ 30%. We assume that Mr. Dowding has made calculations, with both methods, in sufficient detail and number for him to be in a position to judge the relative amounts of time taken with the two methods. We are surprised, therefore, that the rolling-mill designer finds this loss of accuracy unimportant compared with saving the odd 10 min. per calculation. We would have thought that in the design and manufacture of large rolling-mill installations, where several years may elapse between the placing of the order and the final starting up of the equipment, an additional day or so spent in the early stages on calculation would be well worth while, in view of the added accuracy of the results. We would suggest that if an overall accuracy of $\pm$ 30% is all that is required, a much simpler method, in which no allowance is made for tension, would be sufficient. Our own view is that the slightly greater time needed with our method is justified, since, as shown in Part II,[16] an overall accuracy of $\pm$ 10% can be achieved. From remarks made by Mr. Sims in which he indicates that he has derived new equations, to be published elsewhere, it would appear that he also is not entirely satisfied with the equations put forward in the paper by Hessenberg and Sims.

Mr. Polakowski questions the validity of the theories of cold rolling, on the basis that the experimental results show constancy of energy of deformation, although in an earlier paragraph he points out that the total energy falls as the tension increases. The method of assessing the energy of deformation from ordinary meter readings is far too insensitive for any reliable conclusions to be drawn from such results. There is, in fact, a small but definite drop in deformation energy as tensions are applied. Far from contraverting the theory, the experimental results of Hessenberg and Sims bear out the theoretical predictions very closely, as is shown in Part II. Hitchcock's formula applies only to the case when the distribution of pressure is normal to the roll face. The effect of tangential stress has been considered by, among others, M'Ewan.[18]

The effect of friction is to distort the pressure distribution so that it is no longer symmetrical. For values of the coefficient of friction found in cold rolling, the distortion is not very great, and in the case of the rolling process the distortion is reduced because the tangential stress is not uni-directional.

It is thought, therefore, that Hitchcock's formula is not greatly in error even when tangential stress is present, and it is the only method available that does not involve a prohibitive amount of computation for estimating the elastic distortion of the roll face. We would refer Mr. Polakowski to a paper by Bland,[19] in which he will find a more exact estimate of the actual shape of the roll face. This solution does not depend upon Hitchcock's formula, but it is shown that the error involved by this simpler solution is not important except with very thin strip.

Mr. **W. C. F. Hessenberg** said in reply: The fact that Figs. 2 and 3 of our paper were reproduced in so small a size may throw some light on Professor Ford's difficulty in examining our results. (*These figures are reproduced here, on a larger scale, as Fig. G.*)

Mr. Polakowski has evidently examined these results with some care, and has noticed differences between the actual reduction given in each group of experiments. It was impossible to obtain the exact nominal reduction each time, but the whole purpose of the analysis of variance leading to equation (5) was to separate the effects of tension from those of reduction. The coefficients on the right-hand side of the equations for tension are the coefficients freed from any disturbing influence of variations in reduction. The analysis shows, in fact, that tension does affect the energy to a small degree but not sufficiently for it to be necessary to take it into consideration in the calculation of roll force and torque.

Mr. **Sims** wrote in reply: In preparing our paper for publication, Mr. Hessenberg and I attempted to keep the account concise by including only sufficient experimental results to illustrate the equations under discussion. Publication of the whole of the results obtained in rolling the steel coils would have made the report prolix and would have added nothing to make it more informative and acceptable to the mill engineer. The serious student of rolling is not inconvenienced thereby, since the data omitted are freely available on application.

An error has occurred in transcribing the tabulated experimental data, which Professor Ford has been kind enough to indicate and discuss in detail. The value of torque of 1·14 tons-in. in the penultimate line of data for coil 2, Table II, should read 0·14 tons-in., and the calculated value, printed as 1·05 tons-in., should be 0·05 tons-in.

The factor $(1 + f)$ has been omitted from equation (3) because the forward slip $f$ cannot be calculated with precision,[20] and in industrial practice it rarely exceeds 0·1. Examination of the data in Table II (where experimental values of $f$ are given) shows that no closer agreement between equation (3) and the experimental results will be observed by including this factor.

In deriving these simple relationships for roll force and torque, Mr. Hessenberg and I have attempted to provide the mill engineer with a method for assessing quickly the effects of tension. It has already been mentioned that in applying the calculating method of Ford, Bland, and Ellis a value of the deformed-roll radius must be obtained by a series of approximations, and when questions arise in mill design and operation there is not always time for such elaborate calculations. The field of application of the method of assessing the effect of tension which we propose does not overlap, therefore, that proposed by Ford, Bland, and Ellis; the former is intended for industry, whilst the latter will presumably find its greatest use among students, for whom time is not the first consideration and the complexity of equations is no deterrent.

In reply to Professor Ford's comments on the overall accuracy of equations (3) and (10), these equations were intended only to assess the effect of tension on roll force and torque. The errors involved in calculating the no-tension values should not, therefore, be added to the errors involved in using the equations; otherwise, it would be equally justifiable to say that since the rolling industry uses the 'h.p.hr./ton' method for calculating the no-tension torque and roll force, in which the error may easily be ± 40%, the overall error in equation (10) when applied industrially may be ± 60%.

Mr. Polakowski has suggested that the variations of energy were due not to friction but to the deformation

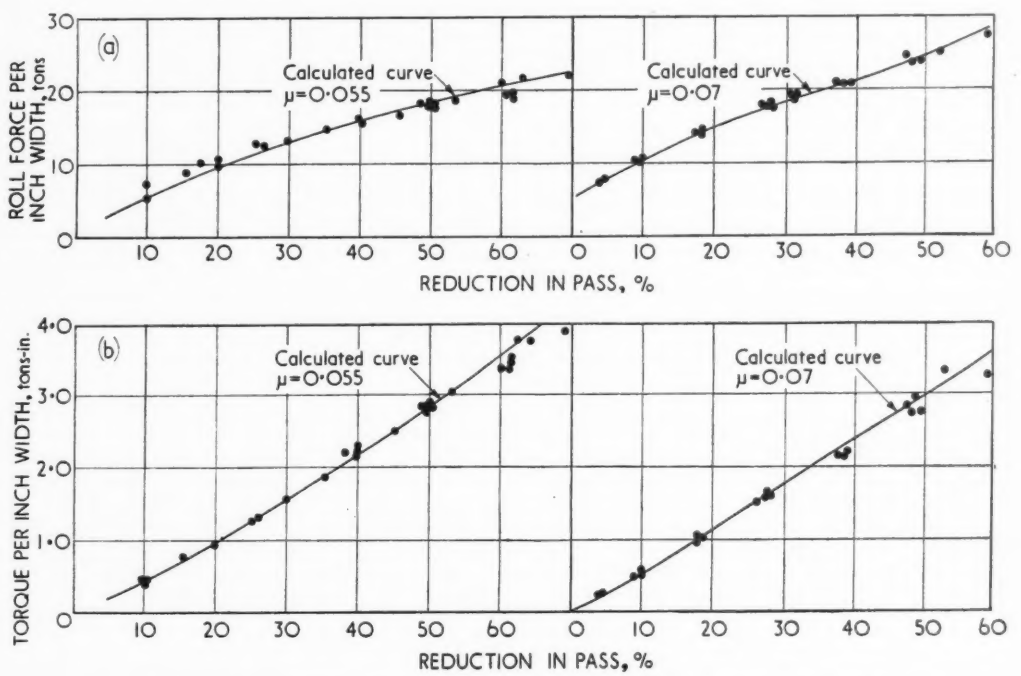



**Fig. G—Experimental values of roll force and torque, plotted against reduction in pass. (*a*) Roll force ; (*b*) torque**

in the roll gap taking place partly in compression and partly in tension. If this is the case, when tension is applied to the strip there should be no variation in total energy when the ratio $R/H$ is varied. In the experiments on annealed material (Table II) $R'/H$ has a value of approximately 80, and on prestrained material the value is about 150. It is clear from experimental results that the ratio $R'/H$ exerts a very considerable effect on the total energy of rolling, and hence it would seem that Mr. Polakowski's suggested mechanism is incorrect.

With regard to the magnitude of the elastic deformation of the rolls when rolling with tension, no attempt has been made to correct Hitchcock's equation for the shear stress at the roll surface. Although the assumptions made by Hitchcock are often considered insufficiently justified, his equation remains the only practical method of allowing for roll distortion. The length of the arc of contact has been measured recently in the B.I.S.R.A. Laboratories by passing a measuring instrument through the roll gap, and from these results it seems that Hitchcock's equation is well within an accuracy of $\pm$ 10%.

Dr. **C. L. Smith:** In reply to Mr. Sims' points, I think that the effect of pin protrusion has been adequately dealt with in the body of our paper. That the impression left by the pin on the stock is the impression only at the point of exit is fully appreciated, but the maximum stress occurs so close to the exit point, in our measurements, and the stress at the exit point is only slightly less than at the maximum, that the impression cannot be appreciably less than that which occurs at the point of maximum pressure. Again, since the correction (*see* Appendix II) for the finite diameter of the pin reduces our observations to ones which could be obtained if the pin were infinitely narrow, it is unnecessary for Mr. Sims to consider the effect of pin protrusion on the observed length of the arc of contact. I will ask Dr. Scott to comment on the increase in the length of the arc of contact to be expected from elastic recovery at the exit point: this is a point on which he has made some calculations. As for comparing the roll force observed with that calculated on the assumption of plane strain, it seemed to us that there was little point in doing this until we were in a position to calculate accurately the contribution to the roll force due to the elastic compression at each end of the arc of contact. There are two opposing factors; the falling-off towards the edge of the strip reduces the value of the roll force below that calculated from an assumption of plane strain, whereas the contribution due to elastic compression increases it above the value so calculated. In practice, it appears that these two factors approximately compensate each other, and this could account for the final point raised by Mr. Sims, that no variation of specific roll force (within the experimental error) has been observed in his experiments for width/thickness ratios varying between 5 and 50.

We agree with Mr. Polakowski that it is a pity that the experiments were not extended to include wider strips, but the rolling mill used would not allow it.

We think it is a pity that Figs. 16*a*, *b*, and *c* of our paper have been reproduced on such a small scale, as it would be very difficult to take accurate readings from these curves if such were needed, for example, to check calculations that may be made at some future date.

Dr. **F. H. Scott** wrote in reply: Mr. Sims mentioned that he has carried out experiments on strips using constant reduction for varying strip widths. When we started this work we attempted to do those experiments to find out the condition where no spread occurs. We were not successful, because of the very point which Mr. Sims made—that roll distortion is dependent on the roll load, and the roll load varies with the strip width. This is important when trying to determine, by means of roll-force measurements alone, if spreading occurs.

The other question is that of elastic recovery, which is also particularly interesting. Some curves which I have calculated have been published elsewhere.[21] Below is given the main outline of these calculations.

The contribution to the total roll force of the elastic stresses between the rolled stock and rolls beyond the 'exit point' $Y$ (*see* Fig. 12) can be estimated by an approximate method. Using the notation in the paper, $h_0$ and $h_0'$ are the thicknesses of the strip at the end of plastic deformation and on leaving the rolls, respectively; $\phi_0$ and $\phi_e$ are the corresponding angles. The principal stresses in the elastic region are taken to be $\sigma_x$ parallel to the direction of rolling, and $\sigma_y$, $\sigma_z$ perpendicular and parallel to the roll axes. The corresponding strains are $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$ The rolled stock is assumed to be isotropic, with Young's modulus $E$ and Poisson's ratio $\nu$.

Assuming plane elastic strain:

$$\sigma_z = \nu(\sigma_x + \sigma_y) \quad \ldots\ldots(1)$$

and therefore

$$\epsilon_y = \frac{1}{E}\left\{(1 - \nu)^2\sigma_y - \nu(1 + \nu)\sigma_x\right\} \quad \ldots\ldots(2)$$

To complete the calculation, the relation between $\sigma_x$ and $\sigma_y$ must be known. The two simplest cases are (*a*) $\sigma_x = 0$ and (*b*) $\sigma_z = 0$, when equation (1) gives $\sigma_x = -\sigma_y$. The true condition almost certainly lies between these and approaches $\sigma_z = 0$ for stock of small breadth.

Consider the case when $\sigma_z = 0$.

Then
$$\epsilon_y = \frac{c\sigma_y}{E} \quad \ldots\ldots(3)$$

where $c = 1 + \nu$. But $\varepsilon_y = (h_0' - h)/h_0'$, and hence

$$h_0' - h = \frac{h_0' c\sigma_y}{E} \quad \ldots\ldots(4)$$

At $Y$, the exit point, $\sigma_y$ is identical with $P$ in the expression given by Orowan[22]:

$$P = K(\phi_0)w_0.$$

Hence
$$h_0' - h_0 = \frac{h_0' cP}{E} \quad \ldots\ldots(5)$$

But at any point on the elastic portion of the curve,

$$R\phi^2 = h - h_0 \quad \ldots\ldots(6)$$

since $\phi$ is small. Thus from equations (4), (5), and (6):

$$R\phi^2 = \frac{h_0' c(P - \sigma_y)}{E}$$

from which it is seen that

$$\sigma_y = P - \frac{ER\phi^2}{ch_0'}.$$

The total elastic contribution $L_E$ to the roll load is therefore given by:

$$L_E = Rb\int_{\phi_e = 0}^{\phi_e = \phi_e} \sigma_y d\phi$$

$$= Rb\left[P\phi_e - \frac{ER\phi_e^3}{3ch_0'}\right] \quad \ldots\ldots(7)$$

where $b$ is the breadth of the rolled strip.

But $R\phi_e^2 = h_0' - h_0 = ch_0'P/E$, and therefore, substituting for $\phi_e$ in equation (7):

$$L_E = \frac{2}{3}b\sqrt{\left(\frac{(h_0' cRP^2}{E}\right)},$$

where $c = 1 + \nu$ for the assumed condition $\sigma_z = 0$.

If $\sigma_x = 0$, then $c = 1 - \nu^2$. If $\nu = 0{\cdot}3$, $c$ may thus vary from 1·3 to 0·9; in most cases it will probably be close to 1·3. The value of $R$ is not easy to obtain, since roll distortion will extend into this region of elastic recovery.

I feel sure that Mr. Bland and Professor Ford may, by now, have developed this further. The discrepancy, which still exists, between the calculated and observed lengths of the arc of contact may, as Dr. Orowan has suggested, be due to very rapid creep. We have assumed homogeneous elastic recovery, and I expect that Mr. Bland, in calculating the theoretical elastic recovery curve at the exit point, will have considered that the strips across recover homogeneously.

Mr. **N. H. Polakowski** wrote in reply: In his first paragraph, Mr. Hessenberg merely restates what has already been said in my paper (p. 343) regarding "the range within which the model (Fig. 15) serves its purpose." The range $0 < P < 2\mu Q$ was considered satisfactory for the purpose, and could be achieved simply. It is within this early stage of deformation that the Bauschinger effect develops gradually from zero in the annealed metal to a maximum, later remaining approximately constant. With a gradually weakening spring $K_1$ the extension curve would be rounded, as Mr. Hessenberg has pointed out, and in that case, admittedly, the curve produced upon reversal would be convex to the strain axis. But this is just the kind of *load/strain* diagram that is usually observed with prestretched ductile metals other than medium- and high-carbon steel, when retested in compression. Obviously, the model was not meant as an end in itself but rather as a kind of pattern, which enabled the experimental observations to be arranged in an orderly and systematic manner. I believe that from this point of view it served its purpose satisfactorily.

The approach of the mechanical metallurgist to the type of phenomena under consideration is naturally different from that of the metal physicist, since the former has usually more direct aims in view. This being so, Mr. Hessenberg's interpretation in terms of the dislocation theory is most welcome. The only relevant opinion so far is that of Nabarro,[23] who stated flatly that he can offer no clear theoretical explanation of why there is a sudden change of rate of work-hardening at about 40% reduction on drawing a steel wire initially heat-treated to 300–350 D.P.H.

I can add little to Dr. Wilson's comprehensive and important contribution. The difficulty with additional hardening upon ageing (or tempering) treatment, in connection with the assumed hardness/internal-energy relation, occurred to me also, since this secondary hardening presumably cannot be associated with a rise of internal energy. The assumption is believed to be valid for a single metal in a single metallurgical condition, and two steels treated to the same hardness in different ways may have different internal strain energies. In the above, a precipitation treatment is assumed to alter 'the metallurgical condition.' Incidentally, some results recently reported[24] confirm that the internal energy in reversed deformation behaves in the manner suggested.

I cannot explain why the lightly tempered martensite did not soften on straining, but in my own experiments (some of which are not reproduced) I did not find a unique relationship between the initial hardness level after heat-treatment and the amount of softening upon subsequent deformation. The hardest material I used was a 0·28% C, 4% Ni, 1% Cr steel showing an initial hardness of 575 D.P.H. falling to 560/565 on compression. I wished to determine to what extent the softening phenomenon is a general one, and later to commence more detailed inquiries, of the kind discussed by Dr. Wilson.

With reference to Professor O'Neill's contribution, I believe that Bauschinger and work-softening effects may affect the hardness test, and that under many conditions the measured hardness may be less than the 'true' one; also, that certain cold-worked metals may soften, even considerably, under cyclic stresses. Some evidence in this respect is already available,[25] and more is expected to be published shortly.[26]

Dr. Hundy raised the important question of directionality in the softening phenomenon. My own experiments yielded similar results, and the decrease of hardness found on the periphery on compression following tensile prestrain was only a fraction of that found on the ends. In softer metals such as copper, aluminium, or even low-carbon steel, no softening could be detected at the sides, under right angles to the direction of compression. This was presumably the reason why the effect remained unobserved for so long.

In regard to Mr. Allison's suggestion, it is, of course, agreed that a considerable amount of heat is developed during rapid upsetting. Whether this is sufficient to cause complete recrystallization of cold-worked iron is not easy to accept on the basis of an isolated test. It may be pointed out that the crystals elongated by cold working in one direction tend to acquire their original, roughly round shape upon reversed deformation without attendant recrystallization. This may not apply to the test referred to, since Mr. Allison's second micrograph [Fig. *C* (ref. 14)] shows much smaller crystals than the first. More evidence of this kind would be required before his concept can be accepted. I may recall that Andrew recently has largely abandoned the theory of austenite formation along the slip planes upon cold working.[27]

I would like to draw attention to an omission on my part in the text of the paper. The hardness tests were carried out on aluminium with a 5-kg. and on other non-ferrous metals with a 10-kg. load on the indenter.

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**Discussion on—**

# AN EXPERIMENTAL FURNACE FOR THE INVESTIGATION OF OPEN-HEARTH FURNACE PROBLEMS

## Part V—Experiments with the Venturi Port and Modifications Thereof*

*By J. F. Allen*

## Part VI—Summary of Results and their Application in Practice†

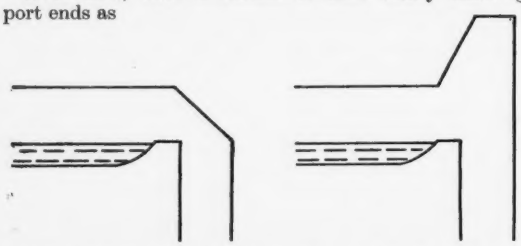
*By J. R. Hall and A. H. Leckie*

Mr. **J. F. Allen** (Steelmaking Division, B.I.S.R.A.) presented Part V.

Dr. **A. H. Leckie** (Head of Steelmaking Division, B.I.S.R.A.) presented Part VI, and conveyed the apologies for absence of Mr. J. R. Hall, his co-author.

Mr. **R. W. Evans** (Steel Company of Wales, Ltd.): The combustion aspect of open-hearth design is now one of the chief subjects of steelmaking research in this country, and the work already done, exemplified in these papers, puts British investigations in the forefront of the international field.

Even now, with advocates of such widely differing port ends as



problems obviously remain, and open-hearth designers and operators are anxious to know which type of construction will give highest outputs and lowest fuel consumptions, and also the best compromise that can be achieved between the ingoing and outgoing ends of the furnace.

Sir William Siemens' invention of the open-hearth furnace was quickly followed by many revolutionary ideas in port design, but about 1905 the furnace began to settle down to a basic design, which persisted until the single-uptake design was advocated by Dr. Leckie.

The objects of research in this field are now clearly defined, *i.e.*,

(i) Attainment of the highest possible flame temperature without undue wear of the brick structure

(ii) Maximum transfer of the combustion heat to the charge.

Often the refractories have to be preserved at the expense of the best design for heat transfer.

The use of driven fuels, *i.e.*, oil, tar, and coke-oven gas, with their high initial velocities and better preservation of flame direction, in general results in simpler furnace designs, which, nevertheless, give high heat transfer together with good refractory life.

Flame temperatures are dependent, apart from the port design, on high combustion air temperature. The introduction of recording suction pyrometers to measure this will be invaluable to the open-hearth operator.

Air infiltration can be a serious source of loss of air preheat, which can render even the best-designed furnace sluggish; modern plants are now designed with plenty of room round the furnaces so that maintenance of insulation and sealing of brickwork are greatly facilitated.

Modern checkerwork, designed for steam blowing and with larger vertical apertures, now lasts much longer and gives consistently high air temperatures.

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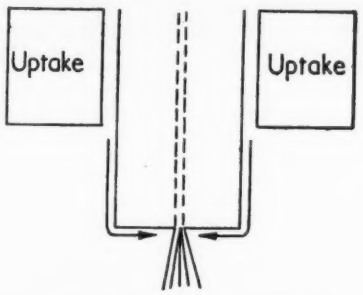
* *J. Iron Steel Inst.*, 1952, vol. 170, pp. 37–44.
† *Ibid.*, 1952, vol. 170, pp. 44–48.

At the Steel Company of Wales we have 200-ton furnaces that Dr. Leckie would describe as of good old-fashioned design ; they have two large uptakes at each end and are thoroughly insulated and sealed below stage. Although they work with high metallurgical loads and are not of single-uptake design, these furnaces achieve extremely low fuel consumptions. One of the reasons for this may actually be the presence of the dog-house. The layout is shown in the diagram :




The hot air, after rising through the uptakes, reaches the nose of the hot brick dog-house. At this point, the suction effect of the high-velocity jet pulls the air round the corners in the direction of the arrows so that the hot air hits the jet at high velocity and at right angles to its direction, which results in very fast mixing. This is put forward as a theory to account for the high performance of these furnaces.

One looks forward in anticipation to the continuance of this work on the Sheffield model furnace.

Dr. **J. H. Chesters** (The United Steel Companies, Ltd.): Most of the open-hearth furnaces today still look extraordinarily like those of 50 years ago, and would still do so, even with the changes recommended by Dr. Leckie. We do, however, have one great advantage over our predecessors, *i.e.*, the possession of a great deal of fundamental information, such as has been provided in parts I–VI of the present work. To this can be added the work done at Battersea on mixing, and our own work on flow patterns. There are now several laboratories in the country capable of trying out radically new ideas on a small scale, and with these facilities we should, I consider, set our objectives rather higher. An increase in output rate of 10% is most helpful, but as research men we should be aiming at 100% improvement.

The criteria normally used to judge success are output rate, fuel consumption and refractory wear. To achieve better figures, we should go for far more intense combustion, combined with better heat-transfer and flow-pattern control, that will protect the refractories. In seeking any radical change, considerable assistance may be obtained from the jet engine, where combustion intensities are hundreds of times as high as in the open-hearth, and yet the combustion chamber is only made of steel. Admittedly great amounts of excess air are used, but we have already demonstrated in our laboratory that excess air is not essential, and that there is no difficulty in using a jet-engine device to achieve very high furnace temperatures. Incidentally, it is interesting to note that whereas in some open-hearth furnaces, *e.g.*, the Maerz type, the recirculation is outwards, in the jet engine recirculation is similar but in reverse.

The problem of transferring the heat is much greater, but it may prove possible eventually to release it inside the scrap, as we do with the arc furnaces, by burying the electrodes. The refractory problem may be solved by the use of all-basic construction, although this is already having to compete with aerodynamic solutions of the same problem.

A generalization that can be made is that when in the present furnace the jet of fuel hits the bath, most of the subsequent high-speed flow is over the walls. This is the precise opposite of the condition we desire, since it is these high-velocity gases that carry the fluxes, which in turn slag the refractories.

The small points that I think should be made in connection with all this work are :

(i) In the model work reported the furnace is not reversed. In actual practice gas-port size may have as big an influence on the exit end as on the entry end, since it determines in part the partition between the waste gases passing through the gas and air checker chambers and consequently the preheats on the return cycle.

(ii) The present work refers to producer gas and similar fuels. The same considerations would not apply directly to oil firing, where there can be ample energy in the oil/steam mixture to give entrainment, regardless of the particular design of port used.

Mr. **M. W. Thring** (B.I.S.R.A.) : There are three fundamental properties of flames with which we are concerned: (i) flame length—where it starts and where it finishes ; (ii) vertical flame position—the angle downwards, how high up it is over the bath and how well it keeps down on the bath, and (iii) the heat-transfer factors of emissivity and convection.

Scaling down upsets emissivity similarity, and in this respect Dr. Leckie's model is not good. The effects shown in Fig. 8 are mainly due to alteration in the position where combustion finishes ; it is primarily a question of flame length, although it may also be a question of flame angle.

Flame length can be determined by putting water-cooled gas-sampling probes in with different ports and seeing where the combustion finishes, or by using the cold-air or water models. When this has been determined, however, the fundamental question remains of whether the flame should be made shorter or not. Some years ago, Dr. Chesters and I concluded that the producer-gas flames at that time were too long. The flame can be made too short in an open-hearth furnace, however, and I think that the type of flame described by Dr. Chesters will be much too short. There is, however, an optimum flame length, and in general flames are too long.

One of the main functions of the air-model work that Mr. Newby is doing is to show how to control flame length. Are the tremendous effects obtained by Dr. Leckie with heat transfer due to flame length, or can they be ascribed to flame angle as well?

It is time, as a result of Dr. Leckie's work, that a proper experiment was done on an open-hearth furnace. We are building up knowledge on how to adjust and control flame properties, but we have never done an experiment as a result of which the effect on output, refractories consumption, and fuel economy could be determined when flame length is changed.

Mr. **M. P. Newby** (B.I.S.R.A.) : In the problem of heat transfer there are two general problems : where the heat is coming from, and where it is going to. This work has been a very successful attempt to determine from a model where some of the heat released in a furnace is going to. Cold models should always be built in collaboration with this type of work, because they show easily where the heat should be coming from. A cold model can predict quickly and easily where a flame should be inside the furnace, and can give an idea of its size and rate of combustion.

The connection between hot and cold models is still largely inferential ; we have no exact measurements between the two. In future work on similar lines there should be closer co-operation between the workers in the two fields, to give a clearer interpretation of the results in terms of actual flame conditions. The work being done at Ijmuiden at the moment on flames, which has been followed up by cold-model work at Battersea, might be a pattern for future work.

Dr. **D. F. Marshall** (Park Gate Iron and Steel Co., Ltd.): In a mill furnace, where the system is almost air-tight, material benefit would be obtained by applying fuel/air ratio control. When checkers, reversing gear, and lengthy flue systems become part of the furnace build, as is the case in an open-hearth furnace, the picture becomes more doubtful. Mr. Allen has been optimistic in drawing conclusions on the use of fuel/air ratio in an open-hearth furnace, based on work on a model that was, in essence, a typical mill furnace.

American furnaces started originally with fuel/air ratio as a No. 1 control, but in most cases that has now been dispensed with because that control has not fulfilled the anticipated purpose. The best advantage of fuel/air ratio from an open-hearth furnace is to be obtained when it is used in conjunction with furnace pressure control.

Dr. Leckie, in discussing fuel/air ratio, mentioned the possibility of having a variable setting, *i.e.*, a different set of conditions for a silica furnace than for a basic furnace. There is also some evidence that there is a better chance of succeeding with fuel/air ratio on a high scrap process than on a high hot-metal process ; in both this country and in America, running on an average of 50% hot metal, most furnaces work on a one- or two-level air control and not fuel/air ratio.

Have the authors considered, in the application of central uptakes, what is the effect of the size of the furnace? The Americans have tried central uptakes in a modified form on large furnaces of 150–200 tons, and in many cases the result has been the reverse of that anticipated ; fuel consumption has increased and rate of output has decreased. In the United Kingdom, with furnaces of 50–100 tons capacity, the results are opposite. Has the actual furnace size, therefore, any effect on the benefits of using a central uptake ?

Air infiltration is a challenge to furnace designers. Modern American plants and the new South Wales plant make accessible all the vulnerable parts of the furnace, but in many plants in this country the vital parts of the furnace cannot be reached. In designing a new plant, one of the first steps is to make the furnace accessible, so as to keep air infiltration to a minimum.

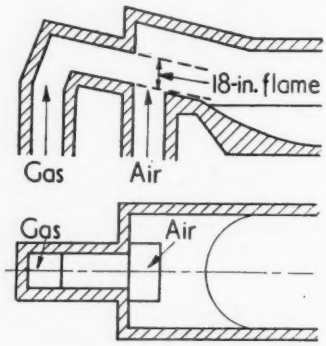
Mr. **J. E. Pluck** (Steel Peech and Tozer) : The model shows a furnace with a flat hearth ; would it be possible to simulate an actual furnace by putting in water tanks with a hump in the middle to represent the average shape of scrap when partly melted ? Such a condition is an important part of the furnace programme. The melting condition is where the maximum heat must be put into the bath. The scrap would, moreover, change the flow patterns, and heat transfer would be different from that shown in the paper.

The steep ramp that has been advised, although it can give very good results, would be, with a ramp of 60° from the horizontal, difficult to build, and more difficult to maintain. Its life might be short, and, if it wore away at the tip, the conditions would be very different from those which the model suggests.

On most furnaces the doors do not really shut, so that to obtain high pressure, with consequent improved heat transfer, this must be remedied. The doorways, and all round the ends and expansion joints, and underneath the roof and skewback, are all generally open positions.

Perhaps the only furnace with a single uptake and producer-gas fuel is one that we built with Mr. Pearson, which worked very well. Its roof life was remarkable. The previous two-uptake designs on that furnace gave trouble, and the design of the furnace was limited by the end binding construction. This gave us considerable trouble down below in the uptakes and on the slag arches before we put in the single-uptake furnace ; when we put a single uptake on the same furnace we still had similar troubles on the uptake and bottom of the slag arches.

With the gas flame coming at the end of the furnace, as on the Maerz furnace, the flame is 2–2½ sq. ft. in area with a thickness of about 18 in. It has to come down on to the bath, and must therefore come over the end of the furnace, as shown in the diagram :




We could not lift the flame very much, or it would not come down on the metal, and so the bottom of the flame edge caught the end bank, which tended to be burned away ; we once had a breakout because of the bad condition at this point. Nevertheless, the output went up, the roof life was improved, and in every other way the furnace was a complete success. For these reasons, however, we did not continue with that shape with gas firing. We are now trying it with oil firing, and we think that it will be successful.

## AUTHORS' REPLIES

Mr. **J. F. Allen** (in reply): We agree with Mr. Thring that the model on which we have worked at Shelton shows us the effect but not all the causes, so much so that the new model in Sheffield has been built to work at a higher temperature range in order to examine the three fundamental qualities which he mentions, *i.e.*, flame shape and size, emissivity, and temperature. Omission of these measurements was a shortcoming of the work at Shelton. Our terms of reference for this work were, however, ' the effect of operating conditions and port design on heat transfer.' Within this framework you have seen certain modifications that can be made; we are going to repeat some of this work in Sheffield, but we are also going to measure the flame emissivities and temperatures.

In answer to Mr. Pluck's question about the flat bottom, as distinct from humps in the middle, such as occur while the furnace is being charged, that is not the critical period. It is fairly easy to get good heat transfer during the charging period because of the difference in temperature between the flame and the charge. Complicating the hearth would, moreover, add immensely to the difficulties of measuring heat transfer

accurately. Conditions giving good heat transfer to a flat bath will also almost certainly apply to a heaped-up contour.

On the question of the central air uptake, there is another fact, brought out by Dr. Chesters. Each of the groups mentioned has its distinctive flow pattern, and, although in the case mentioned there was burning on the edge, it is likely that, because of the flow pattern round the central uptake, there was a concentration of fluxes on the exhaust cycle at this position.

As far as the furnace pressure is concerned, we agree with Mr. Pluck: it is for the engineer to get the structure air-tight. The higher the furnace pressure the better.

Dr. **A. H. Leckie** (in reply): Practical men probably think that the scientists are still very hazy in their ideas, since at one moment they recommend one shape and at another something quite different. The fact is that the simple box-type structure with single uptake is giving very good results, although, from the model, a combination of steep-ramp Venturi roof with a single uptake looks even better. I hope that someone will try the latter to see whether it is better in full-scale practice; if it is, we shall have a stronger case for recommending it for general adoption.

Both Dr. Chesters and Mr. Evans point out that a high-velocity oil jet will draw to itself sufficient air for combustion under almost any conditions, and the advantage of a single uptake in getting rapid combustion is not so marked. Nevertheless, the single uptake has advantages from the point of view of economy in brick-work and general simplicity. Mr. Evans draws attention to the excellent results at the Abbey plant with the conventional doghouse and two uptakes, but might he not have obtained equally good, or even better, results with a simple box design, involving the use of fewer bricks and being cheaper to build ?

Dr. Chesters spoke of the radical improvements which may be derived from using jet-engine techniques. We must, however, remember there is a limiting 'Carnot' efficiency in an open-hearth furnace, and, although that is much higher than is being attained now, the efficiency attained now in relation to the 'Carnot' efficiency is not as bad as if taken as an 'absolute' efficiency. I should like to see in practice one of these 'jet engine' furnaces on a larger scale, but surely if intense combustion in a mass of scrap is desired, as in the electric furnace, it would be logical to put a few 'jet engines' at the bottom of a cupola-like structure. The trouble is that iron will burn more readily than carbon monoxide at melting temperatures. In the open-hearth, everything gets covered with oxide or slag and is protected fairly quickly, but in a radically different furnace with intense combustion within the scrap, there might be too much burning of iron; this does not take place in an electric furnace because combustion air is not present.

The measurements that Mr. Thring suggests are to be taken on the new model in Sheffield.

I do not see why a difference in the air/fuel ratio should be necessary for hot and cold metal practices. Whether the charge is liquid or solid, heating should be effected as efficiently as possible. More air may be needed for oxidation, but one can oxidize with ore; is it as necessary as Dr. Marshall suggests to vary the air/fuel ratio according to the hot metal percentage ?

Single-uptake size is most important. As far as I know, the small proportion of single-uptake furnaces that have been disappointing have had the single uptake too big. In those circumstances, combustion may take place too early, so that the incoming end of the furnace will be too hot and the outgoing end too cold. In several cases where a very large single uptake has failed, a cure has been found by narrowing it down and making it smaller. There is no need at all to make the uptake any larger than is necessary to carry the required amount of gases at the pressures or draughts available.

I agree that the troubles with the only single-uptake producer-gas furnace yet built were peculiar to that furnace. Mr. Pearson and Mr. Pluck were both well aware of what might be done to overcome these troubles, but it was not possible to do it owing to structural and other shop limitations. I would again make a plea for somebody with a producer-gas-fired furnace, but without the same structural limitations, to try a single uptake and embody the various modifications that would get over the troubles to which Mr. Pluck referred.

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## Joint Discussion on the Papers—

## MEASUREMENT OF AIR INFILTRATION IN OPEN-HEARTH FURNACES*

*By R. Haynes, B.Sc.*

## AERODYNAMIC FACTORS ASSOCIATED WITH THE WEAR OF OPEN-HEARTH FURNACE ROOFS† *By J. A. Leys, B.Sc., and E. T. Leigh*

Dr. **A. H. Leckie** (Head of Steelmaking Division, B.I.S.R.A.), who presented the paper by Mr. Haynes, said that Mr. Haynes had now left B.I.S.R.A. Much additional work had been done since the paper was written, and it would be reported in due course. The importance of the work had been emphasized still more by the recent work of Marsh in America, which showed how infiltration could reduce preheat, and the substantial effect of such a reduction upon output.

Mr. **J. A. Leys** (B.I.S.R.A.) introduced the second paper.

Mr. **M. W. Thring** (B.I.S.R.A.): I strongly agree with Mr. Evans that until excess air is properly measured and controlled on the open-hearth furnace, there can be no fair comparison between two furnaces. That is why Mr. Haynes's paper is very important: because he is concerned with the air which really goes through the

* *J. Iron Steel Inst.*, 1952, vol. 170, pp. 149–152.
† *Ibid.*, pp. 336–342.

furnace and not with the air that appears to go through it. I should like, however, to see that work carried further, to the measurement of the quantities flowing in the downtakes as well as in the uptakes, and the use of the oxygen meter on the open-hearth furnace showing always the genuine excess air in the flames as they leave the furnace. Until we have regular measurement of preheat and oxygen in the downtakes, the comparison of open-hearth furnace port design and other things will always result in erroneous conclusions, because knowledge of these measurements is essential in achieving the maximum possible flame temperature, and therefore the greatest output and the best fuel consumption. The paper is a challenge, for it is time that we designed an air-tight open-hearth furnace.

Mr. Haynes refers to the use of the micromanometer. An electrical micromanometer is being developed especially for Pitot tube work, and, with slight modification, it could indicate the square root of the pressure difference, which is proportional to the velocity, and thus enable a proper mean value for velocity as a function of time to be measured from the recorder chart.

The model technique used by Leys and Leigh is quite suitable for their purpose. It is very interesting to find that erosion occurs at the place where solid particles are thrown out of the model. That suggests that if we knew more about the mechanism of erosion we could take the models even further.

For a long time, I have wondered whether it would be useful to build the inside surface of our models with salt, reproducing the silica bricks, to try to obtain even closer comparison with the real furnace. A water spray would be put in with the fuel stream to dissolve the salt, and the contours of erosion could be measured after running the model for a certain time.

On the question of the similarity of these models, Leys and Leigh have used a more trustworthy method than the purely theoretical one. After calibrating the model system against the original furnace, they have made only small changes on the model, and are therefore able to predict more certainly the corresponding results on the real furnace.

Mr. **J. W. Till** (John Summers and Sons, Ltd.): The work described by Leys and Leigh was one of many investigations sponsored by the late Mr. F. L. Robertson, and we have to compliment B.I.S.R.A. and the two authors, in particular, on the very efficient way in which they have carried out our request. Mr. Leys has emphasized that the model technique, properly calibrated and carried out, will correlate with the findings on the actual furnace. The results of tests on the model of particle deposition and the location of areas of severe wear on the actual furnace agreed exactly; and, following suggestions obtained from the model results, for the alteration of burner angle, back wall, and single air uptake, we were able to reduce the effect of the deep gouge along the back wall.

For other reasons, mainly of combustion and manipulation, we were not able to do very much with the burner. The main modification that we made was to straighten out the back wall; and, although we have not made it vertical, we have reduced the severe wear. Wear still occurs there—as it must from that type of furnace—but it is not the deep gouge that we were getting formerly. We were able to put in a hot patch over the week-end, which gave us a roof life of 28 weeks. Subsequent rebuilds of the furnace caused us to merge the two uptakes, producing—virtually—a single-uptake furnace, which has maintained that improvement in roof life; in fact, a roof life of 30 to 33 weeks, including the patch, has been known.

It is obvious, from our practical experience of this model technique, that the proper correlation between the furnace and the model has provided a tool that is of great interest to furnace designers, refractory producers, and steelmakers. We now have at B.I.S.R.A. a scale model of our No. 3 furnaces, which is to be tried out before the actual furnaces go into production.

Mr. **M. P. Newby** (B.I.S.R.A.): The results obtained by Haynes depend very much upon accurate gas-velocity measurements, and such measurements are extremely difficult to carry out when the gases are at high temperatures. The main problem is to invent an instrument to measure such velocities. We have a few ideas, but nothing has yet reached the working stage. We are therefore still relying on Pitot tubes, although we are not sure of their calibration at high temperatures.

To obtain such calibration, we are building a high-temperature wind tunnel in the Physics Department of B.I.S.R.A. Aerodynamically, this will be like a normal wind tunnel in which the waste gases from burning town's gas will produce the high-temperature gas stream in the working section. By measuring the temperature and volume of the gases, we shall know their velocity accurately. We are not expecting any great difference between the behaviour of water-cooled tubes when placed in gases at low temperatures and high temperatures, but we cannot place full reliance on Pitot measurements until the calibration has been carried out.

There is one question that I should like to put to Mr. Haynes. It concerns the actual variation of the coefficient of his tube with pitch and yaw. Haynes states that the variation of the coefficient with yaw was greater than with pitch, but he gives only the value for pitch, the smaller of the two. It would help us to assess the actual value of these measurements if we had at least an estimated figure of the discrepancy with yaw also.

I think that the paper by Leys and Leigh may be regarded as epoch-making, because it is the first paper to deal with a model that has been used to try to predict the pattern of erosion occurring on full-scale furnaces.

Mr. **S. Kruszewski** (United Glass Bottle Manufacturers, Ltd.): In glass furnaces there are no doors to be opened for charging; the feed of raw materials is mechanical, and the furnaces are nearly sealed. It is therefore possible to maintain a positive pressure at the glass level of about 0·05–0·10 in. W.G.

In these conditions of fairly high pressure in the furnace chamber, our common experience is similar to that of Dr. Leckie; *i.e.*, the rate of air flow (metered) at the entry into the air-reversing valve exceeds the amount of air reaching the furnace. Several tests show that this is caused by leakage in the air valves, particularly in those of the flap type; the loss of air can amount to 20% or more.

The leakage at the air valve is highly undesirable, as it spoils the draught and reduces the efficiency of waste-heat boilers.

## CORRESPONDENCE

Mr. **R. Whitfield** (Incandescent Heat Co., Ltd.) wrote: Some years ago, I supervised the erection of a large oil-fired air-regenerative glass tank. Glass tank houses are invariably very dusty. In collaboration with the client, I coated one regenerator externally with two coats of hot silicate of soda, allowing the first coat to dry before applying the second. This sealed the outer surface. Thermometers were carefully placed in corresponding positions on each regenerator; and monthly readings were taken over a period of about a year. The average external temperatures recorded were:

| | Uncoated Regenerator | Coated Regenerator |
|---|---|---|
| At beginning | 108° C. | 110° C. |
| After about 1 yr. | 132° C. | 112° C. |

The monthly readings on the uncoated regenerator had gradually increased, whereas those on the coated regenerator were reasonably constant.

The overall radiation from the walls with a glass-house temperature averaging 70° B.Th.U./sq.ft.hr. was:

| | B.Th.U./sq.ft.hr. |
|---|---|
| Uncoated regenerator | 550 |
| Coated regenerator | 415 |
| Difference | 135 |

The exposed area of one regenerator from top to ground line was 740 sq. ft., causing an additional loss of $740 \times 135 = 100{,}000$ B.Th.U.

At the end of the experimental period, bricks in corresponding positions were removed, sectioned, and examined under a microscope. On the uncoated regenerator the dust had penetrated to a depth of $\frac{3}{4}$–1 in., but on the coated regenerator the coating of silicate of soda was $\frac{3}{16}$–$\frac{1}{4}$ in. deep.

The porosity of bricks is not considered to be of much importance, but it does play a very important part. The porosity of firebricks is 19–38%; that of insulating bricks is about 3–4 times as much. The insulating properties are dependent upon the porosity.

Looking at the problem quantitatively, consider the producer gas from one ton of coal. The volume of producer gas is about 150,000 cu. ft. at 150 B.Th.U./cu. ft., *i.e.*, 67 cu. ft. per lb. of coal; the gas, being hot, will have additional sensible heat. The air to burn this gas will be approx. 1·2 cu. ft. per cu. ft. of gas; thus, $150{,}000 \times 1{\cdot}2 = 180{,}000$ cu. ft. of air.

Taking the average air infiltration as 10%, this air has to be heated to 3072° F. (1700° C.); say, an actual rise of 3000° F. With a volumetric specific heat of 0·02, this will mean that $18{,}000 \times 0{\cdot}02 \times 3000$ B.Th.U. of heat must be provided; *i.e.*, 1,080,000 B.Th.U., which equals $1{,}080{,}000/(67 \times 150) = 108$ lb. of coal gasified.

Obviously, this theoretical amount cannot be realized, but it does provide a yardstick that is worthy of consideration. The dust penetration will very gradually increase, whereas the silicate of soda coating will remain constant. In addition, the unknown factor is more susceptible to control.

Another interesting feature was tried, and proved to be of benefit. In regenerators, the checkers are usually 9 in. × 4½ in. × 3 in. standard square: these were altered to standard side arch of 9 in. × 4½ in. × 3/2 in. There was a distinct improvement with the latter brick, because the vertical taper encouraged the flow of the waste gas downwards, thus reducing friction, and increased the turbulence of the air flowing upwards.

Objection has been raised because of the loss of weight in the checkers, which amounts to about 11%. On the other hand, there is better contact of hot gases downwards or air upwards, and the increased turbulence outweighs the loss in weight.

A useful practical experiment could be carried out with two similar furnaces, by setting one with standard square bricks and the other with standard side arch bricks.

## AUTHORS' REPLIES

Dr. **A. H. Leckie** (in reply): Mr. Thring has suggested that flow in the downtakes should have been measured at the same time as flow in the uptakes. Measurements in the downtakes are equally important in studying furnace behaviour, and the reason why these were not made in the present experiments was simply that there was a shortage of the manpower necessary for manipulation. Each uptake requires a suction pyrometer in addition to a Pitot tube, and at this particular time it was not feasible to handle this equipment for four uptakes. However, this has been done in later work, the results of which will be published in due course. Measurements in the downtakes have been made at various earlier times and were, in fact, reported to the 17th Open Hearth Conference before the war.

I would like to draw attention to the desirability of metering waste-gas flow: for instance, by putting an orifice in the stack or waste-heat boiler flue. The amount of information which can be given by continuously recording the volume of waste gas is surely well worth the relatively small amount of trouble that such an operation involves.

The difficulties of determining low velocities by means of a Pitot tube have been stressed in the paper, and the development of a better pressure-measuring device, such as the electrical micromanometer mentioned by Mr. Thring, will be very helpful.

Mr. Whitfield referred to the use of sealing compounds. Some work on these has been done in collaboration with a member firm, but so far the results have not been very conclusive. It has to be remembered that it is only possible to apply sealing compounds to surfaces that are accessible, and as such surfaces are naturally subject to ordinary maintenance, it is not in these regions that the worst cracks occur. One would anticipate that the worst leakages occur when the inevitable cracks develop in inaccessible places where it is not possible to apply sealing compounds. However, more should be done, particularly with all-basic furnaces in which, owing to the nature of the construction, the brickwork tends to be more open.

It is very interesting to hear of Mr. Kruszewski's experience with glass furnaces, which confirms our observations that leakage past air-reversing valves can be serious. Here again we have much fuller experimental evidence in our more recent work, and although it is only reasonable to expect appreciable leakage across flap valves, it is interesting to know that leakage is by no means negligible even with modern types of slide valve. Such leakage may not be serious from the point of view of furnace operation, but it does add to the difficulties of more precise control.

Mr. Newby has emphasized the difficulties of Pitot work in furnaces, and the new high-temperature wind tunnel that will soon be completed in Mr. Newby's department will be of great assistance in calibrating the equipment used in such measurements.

Mr. **J. A. Leys** (in reply): I should like to thank the speakers for their kind remarks about this paper, and particularly to thank Messrs. J. Till, R. Jones, and C. H. Bacon, who have been most helpful during this work.

In reply to Mr. Thring's remarks about using salt blocks in a model for obtaining quantitative estimates of erosion, certainly an improved technique is desirable. Experiments are now being carried out on the lines he suggests, and we hope that more precise determinations of wear, not only on the roof but also on other parts of furnace linings, will be possible in the future.

**Joint Discussion on the Papers—**

## THE DETERMINATION OF HYDROGEN IN LIQUID STEEL*

*By R. M. Cook and J. D. Hobson*

## DIFFUSION OF HYDROGEN IN IRON AND IRON ALLOYS AT ELEVATED TEMPERATURES†

*By P. L. Chang and W. D. G. Bennett*

## DISTRIBUTION OF HYDROGEN IN LARGE INGOTS AND FORGINGS‡

*By J. D. Hobson and C. Sykes*

## THE EFFECT OF HYDROGEN ON THE PROPERTIES OF LOW-ALLOY STEELS§

*By J. D. Hobson and C. Sykes*

Mr. **R. M. Cook** (The United Steel Companies, Ltd.) presented the first paper, Mr. **W. D. G. Bennett** (University of Sheffield) the second, and Dr. **C. Sykes** (Brown-Firth Research Laboratories) the third and fourth.

Dr. **L. Reeve** (Appleby-Frodingham Steel Co.): In the early days of work on gases and non-metallics, the original emphasis was on oxygen, with a lesser emphasis on nitrogen, but now hydrogen seems to be the most important of these elements. That is illustrated in the two papers by Hobson and Sykes, and also in other directions, in particular in connection with hydrogen in weld metal.

In the paper by Cook and Hobson it is generally implied that the samples taken from liquid steel and kept in dry ice should be examined within 24 hr. We have found that by careful storage of the box of dry ice in which the samples are stored, putting it into another well-insulated container, the loss of hydrogen, even after seven days (168 hr.), is surprisingly small. The samples can be kept safely for two or three days, provided that due care is taken in the container.

Secondly, we found that the pencil specimen described is a little too small in diameter, and if the steel sample which is being poured is on the cold side there is a danger of a cold shut being formed in the sample, which leads to the sort of error mentioned by Hobson and Sykes in the fourth paper, *viz.*, voids down the centre of the specimen and abnormal results. We have increased the sample diameter from $\frac{1}{2}$ to $\frac{3}{4}$ in. with markedly improved results. The ordinary carbometer test specimen makes a very nice pencil specimen if quenched very quickly in the usual way, but we either use old moulds or deliberately increase the diameter to $\frac{3}{4}$ in.

Apart from those two points this method is now suitable for sampling liquid steel with reasonable satisfaction. What is to be accomplished with the method, and the results obtained, are matters for future report, but the indications are that the method will be very useful and, in fact, has already been used extensively.

Concerning the paper by Chang and Bennett, I assume that in due course we shall get, and in fact we already seem to have, the necessary information to calculate actual diffusion rates in fairly large masses of steel, but that is not definitely indicated in the paper.

There is a reference to anomalous behaviour of the Armco iron specimens (they are called ' Armco iron ' in one place and ' ingot iron ' in another). Was this particular heat of ingot iron, the details of which are given in broad outline, deoxidized ? There are two types, the true ingot iron with no deoxidizer added at all and the so-called Armco iron, which very often has a large dose of Al added to it. We did some work some years ago on the permeation of hydrogen, similar to that described in the paper, and we obtained some interesting differences between thoroughly oxidized and killed samples. There is, after all, in the early stages of permeation, a possibility of the reaction of hydrogen with iron oxide in the steel, which would be entirely different from what happens in an Al-killed specimen. It may explain the curious anomaly of the 400° C. break.

The two papers by Hobson and Sykes have interested me because of the implications of some of their results. The paper on the distribution of hydrogen in large ingots and forgings, in particular, with its implied conclusion that relatively small voids will make a very big difference to the distribution of hydrogen, and thereby explain the segregation results which the authors observed, is very interesting to me, because I have done some work, and presented a paper‖ to the Institute which created, I believe, some controversy, on the influence of the degree of oxidation of a steel, or rather of a weld, on its hydrogen content.

Apart from the influence of iron oxide in solution, I referred to the possibility of voidage, in the sense of spaces round inclusions and other small voids, as being a factor in determining the difference in so-called diffusible *versus* total hydrogen content. Where such voids are present there will be a tendency for hydrogen to enter them and become non-diffusible, and it will only be recovered subsequently by high-temperature extraction. Hobson and Sykes' results have an obvious relationship to the point I made.

That raises a further point which I do not think has been followed up in connection with hydrogen in steel, as opposed to hydrogen in weld metal. In the case of hydrogen in weld metal, where appreciable quantities of non-diffusible hydrogen are present, it is possible to keep the weld sample for a very long period—certainly more than six months in my experience, and I do not see why

* *J. Iron Steel Inst.*, 1951, vol. 169, pp. 24–25.
† *Ibid.*, 1952, vol. 170, pp. 205–213.
‡ *Ibid.*, 1952, vol. 170, pp. 118–122.
§ *Ibid.*, 1951, vol. 169, pp. 209–220.
‖ L. Reeve, *J. Iron Steel Inst.*, 1945, No. II, p. 385P.

it should not be several years—and still determine the non-diffusible hydrogen by ordinary vacuum extraction. In ordinary pieces of steel, where the question of non-diffusible hydrogen has not received the same detailed attention, nobody, so far as I know, has taken solid steel samples after a long period, say six months or a year, and determined whether large quantities of hydrogen are evolved again on vacuum heating. The results of Hobson and Sykes suggest that where voids of any type are present, there should be a fair amount of non-diffusible hydrogen in these samples even after a long period.

The second paper by Hobson and Sykes provides the background information to explain what is well known in most test shops in this country, *viz.*, that if there is any doubt about the ductility of a test specimen it is wise to delay the test. It is known definitely that where there is marginal ductility, quite marked improvement may be obtained if the steel is retained for a reasonable period before testing.

We have always assumed this improvement to be due to loss of hydrogen. We know that if large specimens of ordinary carbon steel are kept under mercury for a period of weeks, they are still giving off gas which is substantially hydrogen, and the improvement in ductility is no doubt due to the same phenomenon as is reported in this paper.

The authors have reversed the procedure; they have pumped hydrogen into samples of normal ductility. It has been suggested that, although hydrogen is given off by a carbon steel over a long period, and although its ductility may improve during this evolution, it does not follow that the two changes are related; they may be two independent phenomena occurring simultaneously. This paper, however, shows that the reverse is also true, and that if hydrogen is forced into the steel the ductility drops; that, in my view, clinches the matter.

The fact that no hairline cracks were found in any of the samples may be disappointing, but it is not entirely unexpected. There is some relationship between the cracks formed in the hardened zone of welded alloy steels and hairline cracks. It is now, I think, thoroughly established that cracking in the hardened zones in welded alloy steel is not due to the hardening alone. It has been shown fairly definitely in the last few years that other factors, in addition to local hardening, must be present before cracking takes place, and that the most important of these additional factors is the presence of hydrogen. If no hydrogen, or only a relatively small amount, is allowed to enter the weld, it is possible to have a very high degree of hardness in the welded joint and a very high degree of welding restraint, and yet no cracking takes place; but if hydrogen enters the weld and is allowed to diffuse into the joint, then there is serious cracking.

It seems to me that the questions of hairline cracks and cracking in welded joints are related in that there must be at least two, and possibly three, factors simultaneously present to produce cracking in welded joints: *viz.*, a marked hardening, a certain degree of restraint, and also the necessary concentration of hydrogen present at the right time. Whilst the conditions for hairline cracks are not necessarily identical, again there must be a number of factors simultaneously present, of which hydrogen is only one; the other factors have not yet been clearly established.

Mr. **D. R. Wood** (The Mond Nickel Co., Ltd.): Hobson and Sykes have put forward evidence to confirm earlier impressions that, whilst a simple relationship exists between average hydrogen content and ductility, no such relationship exists with hairline cracking, and the results in their two papers seem to imply that segregation of hydrogen is a more significant factor affecting hairline cracking than is average hydrogen content. It would therefore appear to follow that the hydrogen content of the molten alloy is insufficient evidence on which to predict the formation of hairline cracks on processing.

Considering the effect of hydrogen on ductility, it is surprising at first sight to find that the relationship between average hydrogen content and reduction in area is both simple and reproducible, in view of the marked segregation of hydrogen which has been shown to occur. If segregation causes erratic hairline cracking, why does it not cause ductility measurements to be similarly erratic ? The explanation may be that cracking requires what may be termed 'activation,' such as would be involved in the production of molecular hydrogen in pores, whereas ductility, except in severe cases in which it is also associated with cracking, is dependent on atomic hydrogen in solution and is therefore controlled by diffusion. As long as diffusion is the controlling factor, uniform distribution of hydrogen would be expected, together with a simple, reproducible relationship between hydrogen content and ductility. When segregation occurs, erratic results would be expected. Therefore, the activation may control cracking, and under similar conditions of activation a relationship may exist between cracking and average hydrogen content for any given composition of steel.

It is interesting to note the conclusion of Sims* that, for a given steel SAE 4330, hydrogen contents greater than 0·6 relative volumes, or about 7·6 c.c./100 g., were associated with shatter cracking. The experiments suggested a limiting average hydrogen content below which the forgings were crack-free and above which shatter cracking was to be expected.

Transformation, of course, is a prime mover in hairline cracking, and all the present work on ductility was done by impregnation and without causing the steel to undergo a phase transformation. The segregating influence of transformation was therefore absent.

Hobson and Sykes deliberately chose a method of hydrogen impregnation which would avoid the influence of the effects of prior heat-treatment of the steel, and it might be useful to extend the work by checking the results obtained earlier by Andrew and others on the ductility of steels which had been hydrogen-treated in the austenite range, so as to distinguish between the embrittling effects of hydrogen both segregated and unsegregated, taking care to avoid variations in content and distribution of non-metallic inclusions.

Mr. **J. E. Russell** (English Steel Corporation, Ltd.): In the isobars which Chang and Bennett obtained from Armco iron (Fig. 3) did they repeat those reheating cycles, particularly from 940° C., a number of times, or in fact more than twice ? They obtained repeatable results on reheating and cooling from 400° and 420° C., but erratic results after reheating to 940° C. If they had soaked their specimens for a long time at 940° C. or had continued to give cycles of reheating, they might eventually have come down to a sort of equilibrium curve, because of the scavenging action of the hydrogen at that high temperature. Moreover, did they analyse their samples after these reheating cycles ? It is almost certain that there would be some reduction of the initial carbon content after such high-temperature soaking.

Can the authors explain the fact that on the 10% Mo alloy, as well as the high-Cr one (with over 4% Cr), the divergence from the straight line occurs at the higher

* C. E. Sims, *Amer. Inst. Min. Met. Eng., Proc. Elec. Furn. Steel Conf.*, 1949, p. 302.

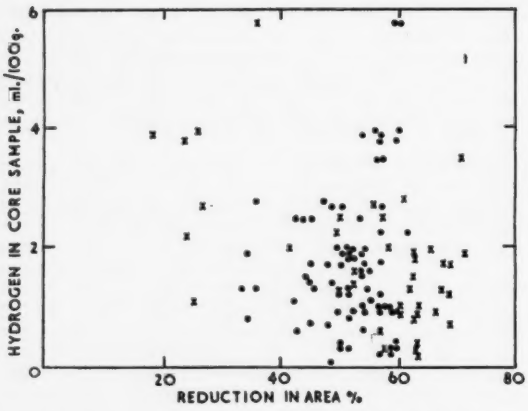


**Fig. A—Reduction in area plotted against hydrogen obtained in the core sample of 3% Cr–Mo rotor forgings**

temperature and not at the lower one, starting at about 600° C. and upwards ? Is that due merely to sluggishness in the $\gamma$–$\alpha$ transformation and, if so, does that indicate that full equilibrium conditions were not reached in their permeation experiments, as is claimed ?

In their paper on the effect of hydrogen on the properties of low-alloy steels, Hobson and Sykes report the examination of a property which is generally known in a less systematic way, the reduction of ductility with raised hydrogen content, but in their conclusions on page 220 they remark that " In forgings, transverse and radial ductility in the body may be significantly reduced if steps are not taken to reduce the hydrogen content below 2 ml./100 g."

Figure A refers to 3% Cr–Mo rotor forgings of about 20–40 in. dia. on the body. After heat-treatment, transverse and radial tensiles are taken on the body, and if they are satisfactory the rotor is trepanned and a hydrogen determination and tensile test are made on the core as quickly as possible. Figure A shows the reduction in area obtained in these tests plotted against the hydrogen obtained in the core sample. The crosses show the results on the core tensile, and the circles the transverse and radial tests on the outside of the body. Thus, the three tests near the top are on one rotor, the cross being the core test and the two circles the transverse and radial on the body.

With the exception of one group on the right, referred to later, the crosses for the core tests show the reduction in area tending to fall with increased hydrogen content, but the outside tests, both transverse and radial, show no such correlation; they are practically independent of the hydrogen content.

The other interesting point about this graph is that below a critical hydrogen content of about 2–3 ml. the core ductilities are preponderantly better than the outside ductilities. Only one cross, with its associated circles, contradicts that remark. On the other hand, above 2–3 ml. of hydrogen per 100 g. the core tests are worse in reduction in area than the transverse and radial tests on the outside of the body. This indicates that there has been considerable diffusion of hydrogen away from the outside of the rotor, probably reducing the hydrogen content on the outside to below 2 ml./100 g., and thus removing any deleterious effect which it may have had on the ductility.

This ' threshold value,' of about 2 ml. seems to depend, partly at any rate, on the actual maximum stress of the rotor itself. All these were heat-treated to about 45–50 tons/sq. in., but the odd one referred to earlier was a relatively soft rotor (about 40–41 tons/sq. in.) and the core ductility is better than in the other two tests, despite the relatively high hydrogen content.

Referring to Hobson and Sykes' paper on the distribution of hydrogen in large ingots and forgings, we have never investigated any one core as thoroughly as the authors have done, but we agree that there appears to be very little systematic top-to-bottom variation of hydrogen content. Their work emphasizes the need for more than one hydrogen sample if any representative figures are to be obtained.

I have not experienced such wide hydrogen variations as those mentioned by the authors; I feel that the arithmetic on page 122 tends to exaggerate these discrepancies, and I rather distrust it. The authors quote the equilibrium solubility in terms of pressure and temperature:

$$S = 0{\cdot}215\ P^{\frac{1}{2}} \exp.\ (-3650/T) \qquad (1)$$

which is true for steel soaked in hydrogen at pressure $P$ and absolute temperature $T$. They postulate a 2-ml. piece of steel, of which 1 ml. is completely solid, the other half containing voids equal in total volume to $10^{-5}$ ml., or quite negligible by comparison. At 900° K. hydrogen diffuses into the voids to give a pressure $P_1$, and the total gas in the 2 ml. of steel is:

$$2S_1 + 1/10^5 \times P_1/760 \times 273/900 \qquad (2)$$

They now use equation (1) to substitute $P_1$ in terms of $S_1$. This, however, is assuming that equilibrium conditions are reached between the hydrogen and the steel. Even if this were true in the immediate neighbourhood of the voids, it could hardly be assumed elsewhere in the centre of the rotor, for if so, and there were *no* voids, the total hydrogen would be $2S_1$ and thus certainly dependent on temperature; but since no diffusion can occur (or at any rate very slowly) from the centre of the rotor, this dissolved hydrogen would be actually constant with temperature. I feel, therefore, that the validity of such a substitution from (1) into (2) would hold, if at all, only in the immediate vicinity of the voids and thus within a volume of negligible amount ($10^{-5}$ ml.) compared with that of the whole (2 ml.).

I am inclined to believe that stresses in the steel (caused by temperature gradients, non-uniform transformations, etc.) may exert some considerable influence on the equilibrium solubility of the hydrogen at a given temperature; if these stresses are tensional the solubility of hydrogen will drop to such a low level that, combined with the reduced ductility caused by the hydrogen, the possibility of the formation of cavities in the form of hairline cracks is very greatly increased. As an example, ' fish-eyes ' are a type of fracture obtained in tensile test pieces of relatively high hydrogen content, which were quite solid at the start of the test. The application of the tensile load is such as to reduce the solubility of the hydrogen and cause cracking to occur as described above.

A side issue on this point is that if the core of a forging should contain internal compressions, thereby holding a relatively large quantity of hydrogen in solution, the sudden relief of stress during trepanning may cause an immediate and considerable loss of hydrogen, probably during the trepanning operation itself, which may cause an underestimation of the original hydrogen content. Moreover, a large forging, however carefully heat-treated, will always contain some residual stress, and a stress of, say, 1 ton/sq. in., trivial from the macroscopic point of view, may be very considerable in its effect from the point of view of hydrogen content, since it will be equivalent to a pressure of about 150 atm. on any cavity which is trying to form.

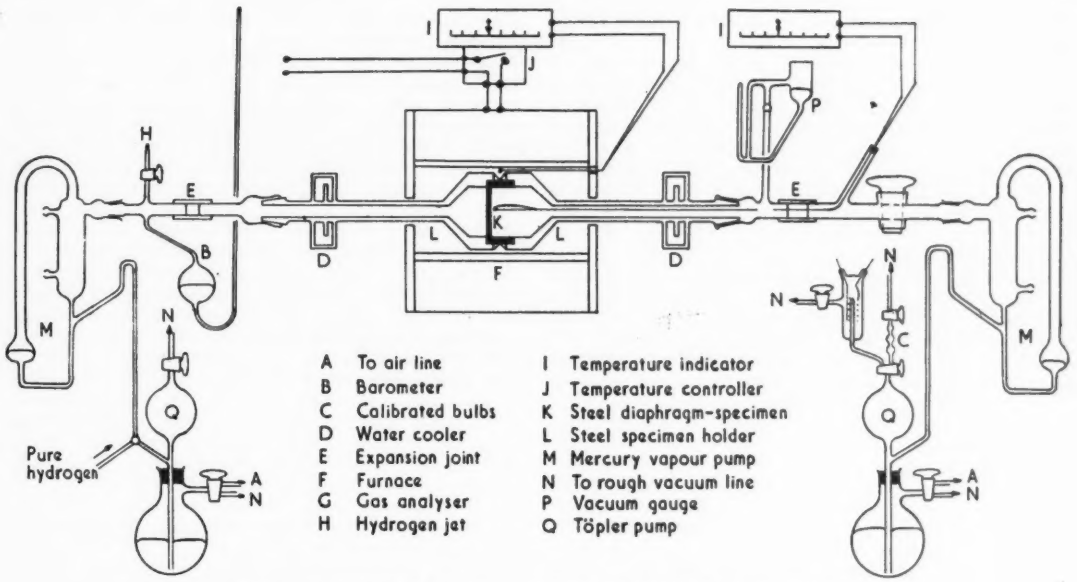


**Fig. B—Apparatus for measurement of hydrogen permeation**

Mr. **J. D. Hobson** (Hadfields, Ltd.): The most striking feature of the paper by Chang and Bennett are the deviations from the theoretical straight line occurring at about 400° C. or slightly lower. In work with which I was formerly associated at the Brown-Firth Research Laboratories, apparatus similar to Chang and Bennett's was employed, but was provided with mercury vapour pumps on each side of the diaphragm. A high vacuum, better than $2 \times 10^{-4}$ mm. Hg, could be maintained on the right-hand side during permeation (Fig. B).

We investigated the permeability of three low-alloy steels and found no deviation (except for the usual α–ν hysteresis) down to 400° C. for a 0·4% carbon steel and a 1% Ni steel, nor for a 3% Cr–Mo steel down to 140° C.

Our results are very similar to those of Bennek and Klotzbach,* who also used continuous pumping and found no deviation when working on iron and low-alloy steels. On the other hand Ham and Rast† reported deviations when using iron, and ascribed these to a new change point. Their apparatus, like Chang and Bennett's, measured permeation by rate of pressure rise. I suggest that the deviations arise when a high vacuum is not maintained, and this phenomenon is probably a function of surface conditions and the experimental method used.

Our results on steels are shown in Fig. C. They are very similar in form to those of Chang and Bennett and of Bennek and Klotzbach. The activation energies calculated from the curves in the α- and ν-ranges show reasonable agreement with earlier workers, and with those of Chang and Bennett (pp. 208, 209):

| Steel | Activation Energy α-Range | ν-Range |
|---|---|---|
| 0·4% C | 19,100 | 38,100 |
| 1·0% Ni | 19,000 | 33,300 |
| 3·0% Cr–Mo | 17,300 | 38,300 |

Most workers agree that the slope of the curve, corresponding with the activation energy, is reproducible. The position of the curve on the graph leads to less satisfactory comparisons. For example, our curve for the 3% Cr–Mo steel (Fig. C) nearly coincides with Chang and Bennett's value for Armco iron, whereas their curves for the effect of Cr would lead one to expect a curve displaced to the left. They say in their paper that their 4% Cr steel seems anomalous, and our results support that comment.

The general conclusion from all the published data*‡ seems to be that all alloying elements tend to decrease permeability as alloy addition increases; but if an attempt is made to cross-correlate the data it is almost impossible to obtain a consistent answer, since although workers agree on the slope of the curves, their absolute values vary by a large factor. I hope that in any future work of this type the absolute values will be carefully standardized, because the present data cannot be applied to quantitative calculations on commercial steel.

The heat-treatment and structure of our alloy steels had a considerable influence on the rate of permeation.

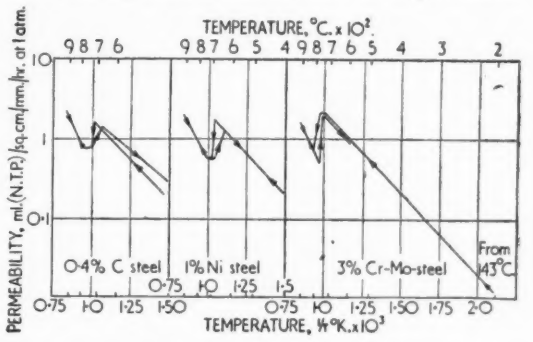


**Fig. C—Permeation isobars for 0·4% C steel, 1% Ni steel, and 3% Cr–Mo steel**

* H. Bennek and G. Klotzbach, *Technische Mitteilungen Krupp*, 1941, vol. 4, May, pp. 47–66.

† W. R. Ham and W. L. Rast, *Trans. Amer. Soc. Metals*, 1938, vol. 26, No. 3, p. 886.

‡ W. Geller and Tak-Ho Sun, *Arch. Eisenhüttenwesen*, 1950, vol. 21, pp. 423–430.

For example, the permeation of the 0·4% carbon steel increased from 1·37 to 1·55 at 660° C. as the specimen spheroidized during seven days. In another case a bainitic structure in the 3% Cr–Mo steel gave 0·400 at 505° C., the same specimen giving 0·467 when the structure was spheroidized pearlite. Since Chang and Bennett's specimens contained small amounts of carbon, their results may be influenced by similar changes.

An important feature of Chang and Bennett's paper is the effect of variation of hydrogen pressure. In similar experiments we found that, provided that a high vacuum was maintained on the exit side of the diaphragm, the permeability varied with the square root of the input pressure, as required theoretically. However, when we reversed the procedure and allowed the pressure to rise in the collecting system, the rate of permeation fell much more than the square-root law predicted, and was approximately proportional to the difference of the cube roots of the pressures. This discrepancy is in the opposite direction from that found by Chang and Bennett. When a high vacuum is not maintained there is a danger that variations of the type found (in opposite sense) by ourselves and by Chang and Bennett, may arise from solution of some of the diffused hydrogen in the metal parts of the apparatus, and by general adsorption.

Finally, I can confirm Chang and Bennett's observation that the equilibrium permeation rate is reached more rapidly in experiments when the desired temperature is being approached by cooling rather than by heating; a similar effect was found in the steel we used.

Mr. **G. T. Harris** (William Jessop and Sons, Ltd.): Cook and Hobson refer to a certain deoxidation practice of the metal samples in the spoon before pouring the pencil samples. It is our experience that this gives no trouble for the final sample just before tapping, but considerable errors are possible at an intermediate stage in the heat.

The authors refer only to the use of a small quantity of Al wire for killing. Some figures which we obtained of the hydrogen level during a heat were about 2·5 ml./100 g. and we considered that these were too low. Three samples at slag-off were therefore taken from a Ni–Cr–Mo steel melted in a basic electric arc furnace. The values obtained using different deoxidants were as follows:

| Deoxidant | Hydrogen, ml./100. g. |
|---|---|
| Excess of ferro-silicon | 2·3 |
| Excess of Al | 2·4 |
| 0·02% Al | 5·6 |

More elaborate work of this type, by Wentrup, Fucke, and Reif,* suggests that 0·02% of Al is the maximum safe addition if true hydrogen values are to be obtained. They attribute the hydrogen loss with Al additions greater than 0·02% to the nucleation effect of the alumina inclusions formed, causing hydrogen to escape during sampling.

## AUTHORS' REPLIES

Mr. **J. D. Hobson** (Hadfields, Ltd.) wrote in reply: In using solid $CO_2$ storage for hydrogen pencil test samples, we have usually advocated analysis within 24 hr. to emphasize the fugitive nature of hydrogen to less-experienced operators. In the original paper of Wells and Barraclough† results were given for samples stored for up to 17 days, with relatively small loss, but we still feel that a minimum of delay before analysis is desirable. We were interested to hear that Dr. Reeve had increased the diameter of the pencil slightly and would agree that this is desirable if the steel is on the cool side. Whilst we have had no difficulty with furnace samples, we sometimes obtain unsound ladle samples, presumably owing to the difficulty of giving the sample spoon an adequate 'warming' in this case. Dr. Reeve's larger test piece will also tend to lessen diffusion losses during storage.

When using solid $CO_2$ cold storage, a well-lagged container is obviously essential to conserve the refrigerant. Our storage boxes are constructed as double cubes, the inner one about 1 ft. cube, with about 4 in. of asbestos-wool padding between the double walls and in the lid. It is essential to bring the test piece into close contact with the solid $CO_2$.

In reply to Mr. Harris: We feel that with only 0·02% of Al added to a sample taken during the boil there is a grave risk that the sample would be unsound. Slight unsoundness leads to high hydrogen values due to the reaction of trapped water vapour and iron, and this appears to have occurred in the example quoted. We would consider a value of 2·5–3·0 ml./100 g. towards the end of the boil as normal; hydrogen pick-up usually occurs under the finishing slag.

Mr. **W. D. G. Bennett** (University of Sheffield) wrote in reply: Most of the comments made on our paper direct our attention to the deviations in the permeation isobars of iron and Fe–Ni alloys at about 400° C.

Dr. Reeve and Mr. Russell have mentioned the possibility of some purification of the specimen by hydrogen, particularly in the early stages of an experiment. The iron from which our specimens were made was not deoxidized in remelting, and the microstructure of the iron as received indicated that no deoxidation had been performed during manufacture. Consequently the soaking at 1000° C., as described on page 207, was regarded as a necessary preliminary to measurements of permeation rates.

Since the effective part of the specimens, *i.e.*, the cylindrical wall, was small, it was not possible to analyse them after the finish of the permeation experiments by the analytical methods at our disposal. As Mr. Russell states, it is extremely probable that the initial carbon content would be reduced.

During our experiments on the ingot iron, the specimen was in the apparatus for about six months and would be in the $\gamma$-range for over 100 hr. Over this period the permeation rates down to about 400° C. were determined a large number of times and were reproducible. A second specimen of the same iron gave results which agreed with results on the first specimen to within $\pm$ 1·5%. We regarded this as evidence that the majority of the change in composition caused by hydrogen took place before the commencement of permeation-rate measurements, and that subsequent purification was too slow to affect the values obtained for permeation rates.

We have no explanation to offer for the increase of permeation rates above those anticipated in the 10% Mo and 4% Cr alloys. In the 10% Mo alloy it may be significant that the composition of the matrix is changing as the $\varepsilon$-phase dissolves and either the change in composition or in the amount of second phase present may influence the rates of permeation.

Mr. Hobson's remarks were extremely interesting and his confirmation of some of the observations made is most welcome.

There are some difficulties attached to his explanation of the deviation in the permeation isobar of iron at 400° C. Firstly, Ham was aware of the possibility that

* H. Wentrup, H. Fucke, and O. Reif, *Stahl u. Eisen*, 1949, vol. 69, No. 4, pp. 117–122.

† J. E. Wells and K. C. Barraclough, *J. Iron Steel Inst.*, 1947, vol. 155, p. 31.

the continuous pumping method may give results different from those given by the rise-in-pressure method. He therefore took care to ensure that for his apparatus the relation between $\log_{10}$ ultimate pressure (on the continuous-pumping method) and $\log_{10}$ rate of pressure increase was linear and had a slope of unity. This relation was established for the apparatus used by ourselves, with ultimate pressures down to $10^{-4}$ mm. Hg, which covers almost the whole range of permeation rates encountered.

Secondly, it does not seem possible to explain the different behaviour of the various alloys investigated. Mr. Hobson's observations on the 3% Cr–Mo steel are consistent with our observations that either Cr or Mo removes the deviation in the permeation isobar. The measurements on the 0·4% C steel and the 1% Ni steel, as well as certain isobars given by Bennek and Klotzbach, unfortunately stop at about 400° C., so that it is impossible to draw any conclusions from them. However, in support of Mr. Hobson's explanation it is to be noted that Smithells and Ransley, using a continuous pumping technique, failed to report a deviation in the isobar of iron down to 200° C.

The sensitivity of permeation rates to structure in steels is well known, but in the present experiments it is likely that the carbon content, particularly after the probable purification during pretreatment, would be too low to cause any variations in permeation rates attributable to structural changes.

Unfortunately, Mr. Hobson has not indicated the temperature at which he investigated the variation of permeation rate with pressure. The cube-root relationship which he gives may arise from giving the same pressure exponent to the forward- and back-permeation processes. The results given in our paper for the effect of back pressure on permeation rates are not based on a large number of experiments, but a conclusion which may be drawn from them is that it is not necessarily true that the pressure exponents of forward- and back-permeation will be identical.

Dr. **C. Sykes** (Brown-Firth Research Laboratories) and Mr. **J. D. Hobson** (Hadfields, Ltd.) wrote in reply: Dr. Reeve has pointed out that, in the presence of voids, steel could contain hydrogen nondiffusible at room temperature. We have evidence that this occurs in practice; for example, some years ago we attempted to make diffusion measurements using a piece of 3% Ni steel billet containing 9·7 ml. of hydrogen per 100 g. The billet was turned down to ¾-in. dia. bar and sampled at intervals with results as follows:

*Hydrogen, ml./100 g.*

| As Turned | Time Elapsed, Days | | | | | |
|---|---|---|---|---|---|---|
| | 2 | 7 | 21 | 42 | 116 | 316 |
| 4·6 | 4·4 | 3·3 | 1·8 | 1·5 | 1·6 | 3·3 |

The appearance of a high result after nearly a year suggests the presence of nondiffusible hydrogen in voids.

In another case we examined portions of a high-pressure ammonia synthesis vessel which had been out of service for 12 years, but had an apparent hydrogen content of over 80 ml./100 g. Investigation showed the hydrogen to be mainly present as methane in small cavities produced by hydrogen corrosion of the carbides.

The presence of either molecular hydrogen or methane in voids may therefore result in a hydrogen content released only by high-temperature extraction.

We agree with Mr. Wood that hydrogen determinations on liquid steel give little indication of the hydrogen content likely to be found in a single determination on a forging. If the liquid steel has a high hydrogen content, however, there will be an increased probability of local high values in the ingot, and increased chances of cracking in the forging. Thus, although individual correlation may not be evident, it will be found on statistical treatment, and in practice there is no doubt that measures taken to reduce the level of hydrogen content, both in the liquid steel and in subsequent heat-treatment, result in a lower incidence of failures.

We feel that the reason for the good correlation of hydrogen and ductility in our work on low-alloy steel tensile properties is to be found in the calculation at the end of the paper dealing with large ingots and forgings. At 600° C., the temperature used for pressure hydrogenation, the hydrogen is almost entirely present in solution and therefore 'active.' It is retained by the water-quench and has little time to migrate to voids before the mechanical test is applied.

We disagree with Mr. Wood that our method of hydrogenation avoids the effect of prior heat-treatment; the method is expressly designed so that hydrogen and heat-treatment can both be varied independently. It would be difficult to apply the method to segregation occurring at the $\gamma$–$\alpha$ transformation, as he suggests, since any subsequent heat-treatment (except quenching) would result in loss of hydrogen and uncertainty in its distribution. Quenching, as used by Andrew and others, would retain the hydrogen but prohibit investigation of the effect of heat-treatment.

We feel that Mr. Russell's criticism of our mathematics distorts our argument; nevertheless, it perhaps needs clarification. We wished to show theoretically that, in an infinitely large mass of steel allowed to reach hydrogen equilibrium at a high temperature, the dissolved atomic hydrogen far exceeds the molecular hydrogen in voids. At low temperatures the reverse holds and the hydrogen at equilibrium is mainly in the voids, with a negligible proportion in solution. The use of 2 ml. of steel merely simplifies the arithmetic. Whilst we realize that such conditions cannot be attained in practice, we think that the trends throw a good deal of light on the segregation we found in ingots and forgings. Mr. Russell considers that residual stresses of about 1 ton/sq. in. may tend to prevent hydrogen from entering voids, but a calculation from Sieverts' law shows that the pressure necessary to maintain 4 ml./100 g. in solution at 20° C. is about 1·2 million tons/sq. in. Whilst it is almost certain that this extrapolation of the law is unjustified, it is also clear that the forces necessary to prevent diffusion could not be provided by residual stress.

We have studied Mr. Russell's graph (Fig. A) with interest. Provided that the hydrogen content is low, the core test (longitudinal) would be expected to show better ductility than the radial and transverse tests on the body. On the other hand, if the hydrogen is high the core piece will have reduced ductility, but the radial and transverse tests from the body will still have low hydrogen and may therefore be superior in ductility to the core. Since the hydrogen determinations do not apply to the body test pieces, correlation on the graph cannot be expected. Even for the core test pieces, unless the hydrogen determination is made on the actual tensile test piece, the segregation present may give rise to wide scatter, as indeed is evident in the data presented.

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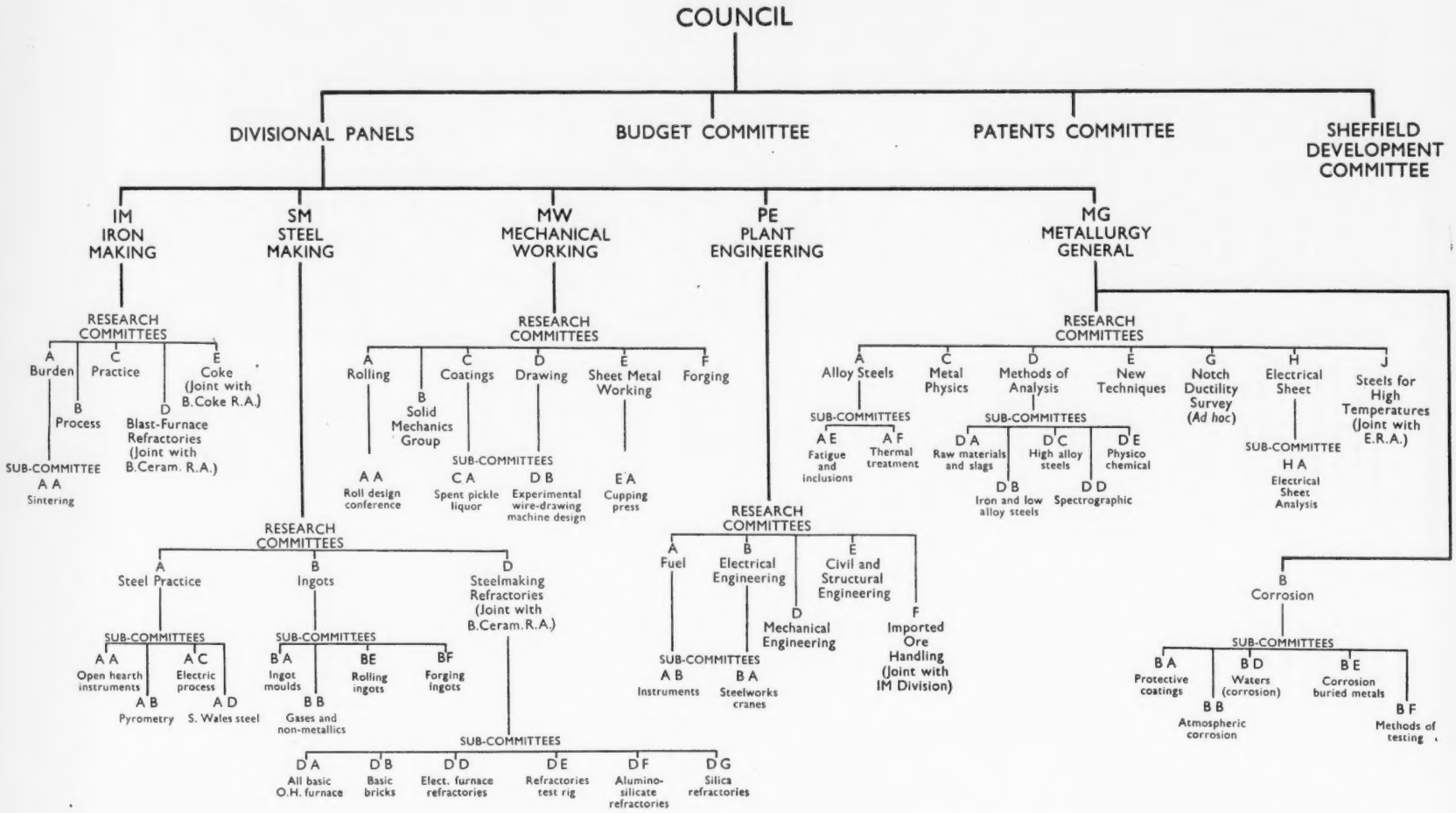

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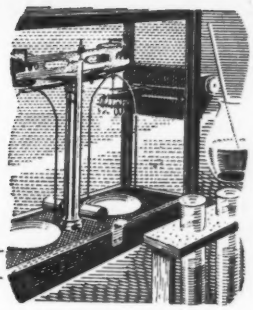

# A Stoichiometric Combustion Method for the Determination of Sulphur in Slags

*By C. J. B. Fincham and F. D. Richardson*

**SYNOPSIS**

A stoichiometric and reproducible method for the determination of sulphur in slags is described. The slag is melted in a stream of $CO_2$, and the $SO_2$ produced is measured. The accuracy claimed is $\pm$ 2%. The analysis time is 30 min. for both open-hearth and blast-furnace slags.

A STOICHIOMETRIC combustion method for the determination of sulphur in slags has been developed in the course of a study of equilibria involving the distribution of sulphur and oxygen between gases and molten lime–alumina–silica slags. As the method appears to be of general interest to those concerned with the analysis of metallurgical slags, a detailed description is being presented here in advance of the main work.

In the conventional method of determining sulphur by combustion at about 1350° C. in a stream of oxygen, only 85–90% of the sulphur is obtained as $SO_2$ and ultimately measured by titration. It has been assumed, but not established, that the remaining 15–10% of sulphur is converted to $SO_3$. This view is in line with knowledge of the thermodynamics of these oxides. As is well known, the trioxide cannot be collected or measured conveniently. It is thus necessary to apply an empirical correction to the measured sulphur, the correction being determined by the combustion of a standard sample in the particular apparatus used. This formation of $SO_3$ can be eliminated almost completely if pure $CO_2$ is used as the combustion gas. Even with untreated commercial $CO_2$, which may contain up to 0·2% of oxygen, it has been estimated that the proportion of slag sulphur converted to $SO_3$ must be substantially less than 0·7%. This gas should therefore be quite acceptable for normal work.

Combustions in untreated commercial $CO_2$ have been used in this laboratory for over a year and have been found perfectly satisfactory. Comparative tests have been made with the usual oxygen combustion and gravimetric methods, with the results described below.

## METHOD

The apparatus used was conventional, consisting of a platinum-wound furnace containing a 1-in. dia. mullite combustion tube. The ingoing combustion gases were measured by a flowmeter. The outgoing gases were passed through a glass-wool trap (to catch dust in the steel analyses), and then bubbled through the absorbent, which was contained in a tall, narrow vessel.

The absorbing solution consisted of 100 ml. of distilled water, 5 ml. of 1 : 4 dilute hydrochloric acid, and 1 ml. of freshly prepared starch solution. Preignited aluminous porcelain combustion boats were used to hold the slag. These were pushed quickly into the furnace so as to keep the influx of air at a minimum. $SO_2$ was titrated, as it was absorbed, with standard potassium-iodate/potassium-iodide solution of suitable strength (usually such that 1 ml. of solution was equivalent to 0·0001 g. of sulphur). As fresh absorbing solution gave a very small blank (about 0·2 ml.) on titration, it was always titrated before use.

The combustion temperature was 1400–1450° C. and the flow rate of $CO_2$ was $\frac{1}{4}$ litre/min. *No fluxes were used.* The weight of slag usually taken was 0·5–1 g., but for the tests with calcium sulphate only about 0·015 g. was necessary. Both the $CO_2$ and the oxygen combustions of open-hearth slags took about $\frac{1}{2}$ hr., but 2 hr. were required for the synthetic lime–alumina–silica slags, probably on account of their greater viscosities. However, $\frac{1}{2}$ hr. was sufficient for $CO_2$ combustions of a typical blast-furnace slag.

Paper CP/17/1 of the Chemistry Department of the British Iron and Steel Research Association, received 20th March, 1952.

Mr. Fincham is on the staff of the Association.

Dr. Richardson is Director of the Nuffield Research Group in Extraction Metallurgy at the Royal School of Mines.

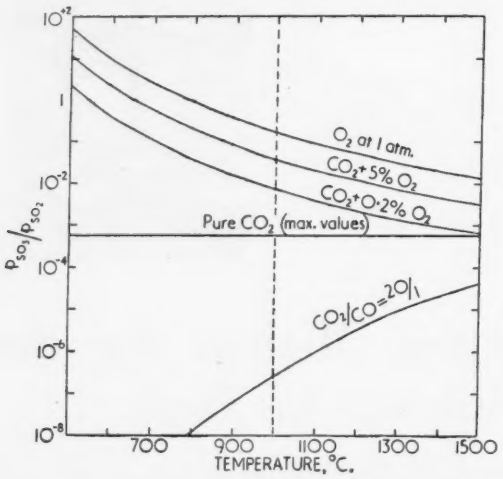


**Fig. 1—The temperature dependence of the *equilibrium* proportions of $SO_3$ to $SO_2$, when both gases are present at small concentrations in various combustion gases. The values shown have been calculated from thermodynamic data† for the reactions:**

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \text{ and } CO + \tfrac{1}{2}O_2 = CO_2$$

## RESULTS

For comparative tests, three different slags were analysed by oxygen combustion and $CO_2$ combustion. Two of these were also analysed by the gravimetric method. Another slag (No. 4) was analysed by the $CO_2$ combustion method, the evolution method, and the gravimetric method. The results are shown in Table I (items 1–4). All the gravimetric analyses were carried out by the Analysis Section of the Metallurgy Division of B.I.S.R.A.

The $CO_2$ combustion results shown in Table I are not corrected in any way. Some of the oxygen combustion results were obtained at an oxygen flow rate of 0·5 litres/min., and some at 0·25 litres/min. The correction factors for these two rates (determined by combustion of a standard steel containing 0·237% of sulphur) were 1·11 and 1·15 respectively. The results for this method are shown both uncorrected and corrected. The gravimetric results were obtained by the normal method, *i.e.*, oxidation of the sulphur to sulphate, separation of silica, and precipitation and weighing of the sulphur as barium sulphate. In the evolution method the slag was dissolved in hydrochloric acid, and the hydrogen sulphide produced was absorbed and measured by the method of Kitchener, Liberman, and Spratt.*

## DISCUSSION

The results obtained by combustion in $CO_2$ agree well with those obtained by the gravimetric method. The results from combustion in oxygen, however, are ½–3½% low compared with those from combustion in $CO_2$. It thus appears that the use of a standard steel to calibrate for slag analysis is not entirely satisfactory.

If the possibilities and limitations of the method are to be fully understood, the thermodynamics of the basic reactions must be considered in some detail.

It can be calculated from thermodynamic data† that at 1400° C. the proportion of $SO_3$ to $SO_2$, in equilibrium with 1 atm. of oxygen, is only about 2 vol. %. The proportion of sulphur lost in an analysis by oxygen combustion is much greater than this, for the equilibrium percentage of trioxide increases markedly at lower temperatures, reaching 15% at 1000° C., as shown in Fig. 1. It is therefore possible for the trioxide to form as the combustion gases cool on leaving the hot zone of the furnace. Since the rate of conversion of dioxide to trioxide decreases as the temperature falls, very large losses of sulphur as trioxide do not occur in normal practice.

Measurements on the distribution of sulphur and oxygen between gas and slag have shown that, from an analytical standpoint, the most favourable equilibrium partition at 1400–1500° C. occurs at oxygen pressures of $10^{-6}$ to $10^{-5}$ atm. (the equilibria at an oxygen pressure of 1 atm. are actually not so favourable). These low oxygen pressures can be conveniently obtained at 1 atm. total pressure by means of a gas mixture consisting of 20 parts by volume of $CO_2$ to one part of CO. As can be seen from Fig. 1, the proportion of sulphur which can be converted to the trioxide in such a mixture is negligible.

However, it is not essential to use a $CO_2$/CO gas mixture to obtain quantitative production of $SO_2$. Combustion can be done in a stream of $CO_2$. The equation for the evolution of the $SO_2$ is then:

$$3CO_2 + (S)_{slag} = SO_2 + 3CO + (O)_{slag}.$$

From this it follows that

$$p_{SO_2} \sim \tfrac{1}{3}p_{CO}.$$

From the $SO_2$–$SO_3$–$O_2$ equilibrium it also follows that, at 1000° C.:

$$p_{SO_3}/p_{SO_2} = 1{\cdot}4 \times 10^{-8}/p_{CO}.$$

The partial pressure of CO will be a maximum when $p_{SO_2}$ is a maximum, and a minimum when evolution of $SO_2$ has ceased. This minimum value will be that corresponding to the dissociation equilibrium of $CO_2$ according to the equation

$$CO_2 = CO + \tfrac{1}{2}O_2.$$

At 1000° C.:

$$p_{CO} = 2{\cdot}4 \times 10^{-5} \text{ atm.},$$

so that

$$p_{SO_3}/p_{SO_2} \text{ (max.)} = 6 \times 10^{-4}.$$

The $CO_2$ curve in Fig. 1 shows that this maximum value is almost independent of temperature. The proportion of sulphur lost as trioxide in a $CO_2$ combustion should therefore be substantially less than 0·06%. As already explained, the commercial $CO_2$ used without further purification contained up to 0·2% of oxygen. For this combustion gas, $p_{SO_3}/p_{SO_2}$ (max.) is $7 \times 10^{-3}$ at 1000° C., the other equilibrium values being as in Fig. 1. In this case the proportion of sulphur lost in an analysis should be substantially less than 0·7%.

It is important to know whether this method of

* J. A. Kitchener, A. Liberman, and D. A. Spratt, *Analyst*, 1951, vol. 76, p. 509.

† F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst.*, 1952, vol. 171, p. 165.

Table I—ANALYTICAL RESULTS—SULPHUR, WT.-%

| Sample No. and Type | $O_2$ Combustion (Not Corrected) | $O_2$ Combustion (Corrected) | $CO_2$ Combustion (No Correction) | Gravimetric |
|---|---|---|---|---|
| (1) Open-hearth tapping slag | 0·342<br>0·331<br>0·335<br>0·324<br>Mean: 0·333 | (Steel factor 1·11)<br>Mean: 0·370 | 0·370<br>0·372<br>0·375<br>0·374<br>0·370<br>Mean: 0·372 | – |
| (2) Open-hearth tapping slag | 0·144<br>0·150<br>0·149<br>0·149<br>Mean: 0·148 | (Steel factor 1·11)<br>Mean: 0·164 | 0·171<br>0·171<br>0·170<br>0·169<br>Mean: 0·170 | 0·18 ± 0·02 |
| (3) Synthetic slag:<br>CaO 47%<br>$Al_2O_3$ 17%<br>$SiO_2$ 36% | 0·251<br>0·248<br>0·249<br>Mean: 0·249 | (Steel factor 1·15)<br>Mean: 0·287 | 0·299<br>0·297<br>0·298<br>0·293<br>Mean: 0·297 | 0·30 ± 0·02 |
| (4) Synthetic slag:<br>CaO 41%<br>$Al_2O_3$ 52%<br>$SiO_2$ 7% | Analysed by Evolution Method | 0·642<br>0·635<br>0·645<br>Mean: 0·641 | 0·622<br>0·627<br>0·624<br>0·627<br>Mean: 0·625 | 0·63 ± 0·02 |
| (5) AnalaR $CaSO_4.2H_2O$ (Theoretical % S = 18·6) | 15·8<br>15·7<br>15·5<br>15·6<br>Mean: 15·65 | (Steel factor 1·15)<br>Mean: 18·0 | 18·3<br>18·4<br>18·1<br>18·2<br>18·4<br>Mean: 18·3 | 18·8 ± 0·15 |

combustion in $CO_2$ includes sulphur which may be present as sulphate in the slag. The authors' equilibrium studies have shown that small amounts of sulphate may be present in slags prepared or cooled under oxidizing conditions. The evolution of sulphate sulphur must follow an equation of the type

$$(SO_4)_{slag} = SO_2 + \tfrac{1}{2}O_2 + (O)_{slag}$$

The corresponding equation for sulphide sulphur is

$$(S)_{slag} + 3CO_2 = 3CO + SO_2 + (O)_{slag}$$

It follows that, provided the sulphate sulphur is less than three times the sulphide, enough CO will be produced by the second reaction to react with virtually all the oxygen from the first. Thus the oxygen pressure will be kept too low to produce any significant proportion of $SO_3$. When sulphate only is present some formation of $SO_3$, with correspondingly low sulphur analyses, is to be expected, even when $CO_2$ is the combustion gas. This was so in analyses of AnalaR calcium sulphate (*see* Table I, item 5).

With calcium sulphate nearly all the sulphur was evolved in 1 min. in the authors' apparatus. From the $CO_2$ flow rate and this approximate rate of evolution the partial pressure of oxygen during the sulphur evolution can be estimated at about 0·05 atm. At 1000° C. the ratio of $SO_3/SO_2$ in equilibrium with such a pressure would be about $3 \times 10^{-2}$. The 3% difference between the results of the $CO_2$ combustion and gravimetric methods is therefore not unreasonable.

If the rate of evolution of $SO_2$ and oxygen from the sulphate had been much slower (as might arise in the analysis of a slag containing small amounts of sulphate in the absence of sulphide), the sulphur lost as trioxide would be very much less. If, for example, the rate of evolution were 100 times slower, the oxygen pressure *arising from the decomposition of the sulphate* would reach a value of only $5 \times 10^{-4}$ atm. This figure is small compared with the $2 \times 10^{-3}$ atm. of oxygen present in commercial $CO_2$. Under such conditions, results with sulphate sulphur should be as good as those for sulphide, and this has been the experience of the authors.

The method as it stands is not satisfactory for the analysis of steels. Tests showed that combustion of a steel with $CO_2$ took over 2 hr. Not only is this far too slow for routine analyses, but in this time normal combustion boats are destroyed by the iron oxide produced.

The accuracy of the method is considered to be ±2% of the total slag sulphur at concentrations above 0·1%, with sample weights of about 1 g. This takes into account the effect of using untreated commercial $CO_2$. It would not apply to slags containing large amounts of sulphate associated with small amounts of sulphide.

## Acknowledgment

The authors are indebted to Dr. J. Pearson for his help and interest which has made the authors' collaboration possible.

# Effect of Specimen Length on the Strength of a Material with Random Flaws

*By K. E. Puttick, B.Sc., and M. W. Thring, M.A., F.Inst.F., F.Inst.P.*


## SYNOPSIS

The statistical strength properties of materials are discussed for tests, such as the tensile test, in which it may be assumed that the specimen fails at its weakest point. The test piece thus behaves like a chain, and the variation of mean and standard deviation of the results of tests with length of specimen depends on the distribution of strengths of individual links. The consequences of two distributions are considered: first, that the distribution is normal, and second, that there is a very small number of links, randomly spaced, whose strength is much smaller than the rest. These correspond respectively to a material homogeneous on the scale of the test and one in which there are defects whose size is small compared with the test length but whose mean distance apart is comparable with it. The former model predicts a continuous decrease in mean test result and standard deviation with increase in specimen length; the latter predicts a continuous decrease in the mean but a maximum for the standard deviation for a specimen length for which the probability of including at least one flaw is $\frac{1}{2}$. Experiments on cold-drawn phosphor-bronze wire show that this model gives a better description of the variation of standard deviation and mean with test length, the mean spacing of the flaws being about 3 in. For such a material it is desirable to take large samples ($\lessdot$ 20) for at least three different lengths.


## Introduction

It is frequently found that the results of mechanical tests on a material depend on the dimensions of the specimens. Where the latter are variable the question arises as to what size of specimen should be chosen, and how many determinations made, to make the most efficient use of the test.

It is often assumed that the relation of mechanical properties to specimen size is a consequence of a statistical distribution of the flaws responsible for failure, there being a greater probability of including a flaw in a larger test piece. It is this approach with which the present paper is concerned. In certain cases of practical importance, notably brittle fracture, other factors may be involved.[1, 2]

It is required, then, to formulate a theory of the influence of specimen size on (*a*) the mean and (*b*) the dispersion of the results of a number of strength tests. Tucker[3] has pointed out that it is necessary first to postulate some mechanism of failure. Thus, in the tensile test it may be supposed that the test piece fails at its weakest point, so that the appropriate model to use in estimating the effect of changing the test length would be that of a chain. In varying the lateral dimensions of the specimen the appropriate model is not obvious; even if the discussion is restricted to purely statistical effects, the theoretical variation of strength with diameter depends on whether the flaws responsible for failure are at the surface or distributed throughout the volume of the material. The question of varying the diameter of the test piece when the weakest-link condition does not hold is discussed in the Appendix.

In this paper the weakest-link criterion is used throughout, so that the discussion will be chiefly relevant to changing the length of test piece in a tensile test. Such considerations will be important in testing material in the form of rod, wire, or strip. The problem considered in the following sections is then essentially that of predicting the mean and standard deviation of strengths of chains from a knowledge of the characteristics of individual links.

Paper MW/B/9/52 of the Solid Mechanics Group of the Mechanical Working Division of the British Iron and Steel Research Association, received 1st May, 1952.

Mr. Thring is Head of the Physics Department and Mr. Puttick is in the General Physics Section of the Association.

### List of Symbols

$\sigma$ = standard deviation of population
$\bar{S}$ = mean strength
$S_1$ = strength of test piece without a flaw
$S_2$ = strength of test piece with one or more flaws
$\mu_2$ = second moment about the mean of a distribution
$\mu_4$ = fourth moment about the mean of a distribution
$\mu_2'$, $\mu_4'$ = moments about a point other than the mean
$\beta_2 = \mu_4/\mu_2^2$
$l$ = length of test piece
$l_0$ = mean distance between flaws
$l_2$ = length of flaw
$n$ = number of flaws in test length
$\bar{n}$ = mean value of $n$
$S$ = standard error = sample estimate of $\sigma$
$r$ = number in sample
$A$ = area of cross-section of specimen
$A_2$ = area of flaw
$r_1$ = radius of test piece.

## THEORETICAL CONSEQUENCES OF THE DISTRIBUTION OF STRENGTHS OF SINGLE LINKS

### Normal Distribution of Strengths of Single Links

Having accepted the chain model, it is then necessary to postulate some form of distribution of strengths

for the individual links. The most obvious assumption to make is that the strengths of links are normally distributed and that the strengths of adjacent links are statistically independent. The problem is then that of finding the mean strength and standard deviation of chains of $N$ links, each in terms of the mean and standard deviation of individual links. In interpreting his experiments on concrete cylinders, Tucker[3] made use of Tippett's solution of this problem[4]; it involves finding the distribution of extreme individuals in samples from a normal population, the number in the sample being identified in this case with the number of links. The variation of the standard deviation with $N$, according to Tippett, is shown in Fig. 1*a* for the range $N = 1$–$1000$, and of the mean for various values of the standard deviation of individual links in Fig. 1*b* ($\sigma_1$ and $M_1$ are the values for a population of single links).

In terms of the usual tensile test, this theory predicts the variation of standard deviation and mean strength of test pieces with length, in terms of the smallest length on which such determinations are made, assuming that the strengths of these units are normally distributed. 'Strength' is taken as any measurement for which the weakest-link theory is appropriate.

The above discussion is probably valid for reasonably homogeneous materials, *i.e.*, those in which the distance between the flaws responsible for failure is very much smaller than the size of the specimen. If, however, there are marked flaws in the material, the mean distance between which is comparable with the length of the test piece, the assumption of normal distribution of strengths of unit lengths is no longer valid.

### Two-Strength Material

We next consider the properties of a chain in which the majority of links have all the same strength $S_1$, but in which there are a very small number of much weaker links of strength $S_2$ occurring at random.

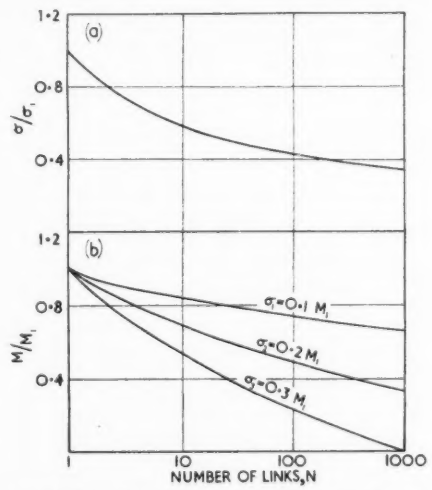


**Fig. 1—(*a*) Standard deviation of strength of chains (Tippett); (*b*) Mean strength of chains (Tippett)**

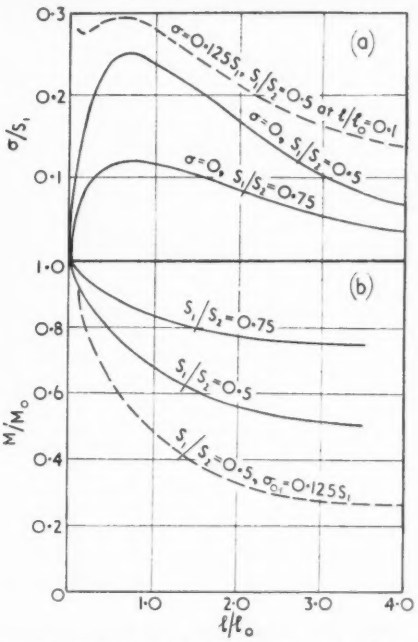


**Fig. 2—(*a*) Standard deviation of strength of material with random flaws; (*b*) Mean strength of material with random flaws**

This is the analogy of continuous material with randomly occurring flaws, the length of which is much smaller than the length of a test piece, but between which the mean distance is of the order of the specimen length. The case in which the flaws are not themselves small is considered in the Appendix.

This chain model was used by Weibull[5] in his theory of the size effect in brittle fracture, which deals with the variation of brittle strength with diameter and, as already mentioned, its validity in that connection is controversial.

Let the length of the test piece be $l$, the mean distance between flaws $l_0$. The probability of including $n$ flaws in the test length is then given by the Poisson formula:

$$P(n) = \frac{(\bar{n})^n e^{-\bar{n}}}{n!}$$

where $\bar{n} = l/l_0$ is the mean value of $n$. Accordingly the fraction of a large number of specimens tested which will be without flaws is $e^{-\bar{n}}$, and the mean strength of a population of specimens is:

$$\bar{S} = e^{-\bar{n}}S_1 + (1-e^{-\bar{n}})S_2 \quad \ldots\ldots\ldots\ldots (1)$$

The standard deviation of strengths is:

$$\sigma = \frac{1}{r}\sqrt{\{\Sigma(S-\bar{S})^2\}}$$

where $r$ is the number of specimens

$$= \sqrt{\{e^{-\bar{n}}(S_1-\bar{S})^2 + (1-e^{-\bar{n}})(\bar{S}-S_2)^2\}}$$

$$= (S_1-S_2)\sqrt{\{e^{-\bar{n}}(1-e^{-\bar{n}})\}} \quad \ldots\ldots\ldots\ldots (2)$$

The behaviour of these functions is illustrated by the full-line curves in Figs. 2*a* and *b*, for two values of

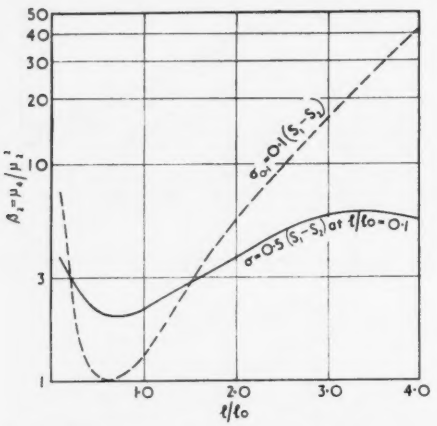


**Fig. 3—Variation of $\beta_2$ for the modified two-strength distribution with specimen length**

$S_1/S_2$, in terms of $S_1$. The standard deviation passes through a maximum at $l/l_0 = ln2$, since this is the length at which half the test pieces contain flaws. The mean strength, of course, decreases rapidly over this range.

It is possible to generalize this simple model to the case in which the strengths of test pieces are distributed so that test pieces which do not contain flaws have one normal distribution; those which contain one or more flaws a second normal distribution with different mean and standard deviation. (This is not the same as postulating a normal distribution of strengths of *flaws*; this would not give a normal curve for the strengths of test pieces containing flaws.)

The total distribution is then a bimodal curve given by:

$$y = \frac{e^{-\bar{n}}}{\sigma_1\sqrt{2\pi}}\, e^{-\frac{(S-S_1)^2}{2\sigma_1^2}} + \frac{(1-e^{-\bar{n}})}{\sigma_2\sqrt{2\pi}}\, e^{-\frac{(S-S_2)^2}{2\sigma_2^2}} \quad \ldots(3)$$

where $S_2$, $S_1$ are now the mean strengths of the test pieces with and without flaws respectively, and $\sigma_2$, $\sigma_1$, are the respective standard deviations.

The second moment or variance of equation (3), defined as:

$$\mu_2 = \frac{1}{r}\Sigma(S - \bar{S})^2$$

where $\bar{S}$ is the mean of the whole distribution, is then:

$$\mu_2 = \frac{1}{r}\left\{\Sigma(S_1 - \bar{S})^2 + \Sigma(S_2 - \bar{S})^2\right\}$$
$$= \frac{1}{r}\left\{re^{-\bar{n}}\,\mu_2' + r(1 - e^{-\bar{n}})\mu_2''\right\} \quad \ldots\ldots\ldots (4)$$

where $\mu_2'$, $\mu_2''$ are the second moments of the component normal curves of equation (3) about $\bar{S}$.

Now $\mu_2' = \sigma_1^2 + d_1^2$ and $\mu_2'' = \sigma_2^2 + d_2^2$

where $d_1 = S_1 - \bar{S}$ and $d_2 = \bar{S} - S_2$

As before $\bar{S} = e^{-\bar{n}}S_1 + (1 - e^{-\bar{n}})S_2$ .....(5)

so that from (4):

$$\mu_2 = e^{-\bar{n}}\sigma_1^2 + (1 - e^{-\bar{n}})\sigma_2^2 + e^{-\bar{n}}(1 - e^{-\bar{n}})(S_1 - S_2)^2 \ldots(6)$$

and the standard deviation is the square root of this. In estimating the effect of change of length of specimens from the population, equation (3), it must be remembered that $S_1$, $S_2$ and $\sigma_1$, $\sigma_2$ will themselves vary with length, as was indicated in Fig. 1, since they are the means and standard deviations respectively of samples from normal populations.* In computing equations (5) and (6) it is therefore necessary to assign fixed values for $\sigma_1$ and $\sigma_2$, $S_1$ and $S_2$, to a particular length. Figure 2*a* (broken line) shows the variation of standard deviation of test pieces with length, assuming that $\sigma_1 = \sigma_2 = 0{\cdot}5(S_1 - S_2)$ at $l/l_0 = 0{\cdot}1$ and $S_1/S_2 = 0{\cdot}5$. The effect of flaws shows as a kink in the variation given by Fig. 1*a*. The mean of the same population is plotted as a function of length in Fig. 2*b* (broken line).

It is not, of course, necessary to assume that the strengths of flawed and unflawed test pieces are normally distributed, but for any other distribution the Tippett extreme-value calculations would have to be made afresh to allow for the effect of changing length on $S_1$, $S_2$ and $\sigma_1$, $\sigma_2$.

### Sampling Errors and the Character of the Two-Strength Distribution

It is clear from the preceding sections that the variations of both standard deviation and mean with specimen length are significant indications of whether or not weak spots exist in the material. Both these parameters, however, are subject to large sampling fluctuations, and it is important to consider these in relation to the non-normal character of the two-strength distribution.

* Unless $\sigma_1^2$, $\sigma_2^2$ are measures of the variance inherent in the test rather than the material, when they will be independent of specimen size. In practice, both test and material will contribute to these variances.

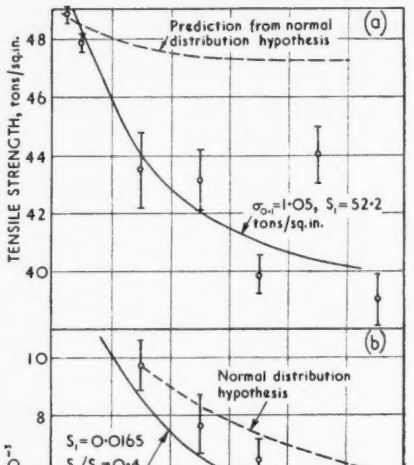


**Fig. 4—Phosphor-bronze wire: (*a*) Mean tensile strength; (*b*) mean strain to neck**

The sampling standard error of the mean is unaffected by the form of the distribution from which the sample is drawn and is equal to $\sigma/\sqrt{n}$, where $n$ is the number in the sample. This statistic, however, does involve the standard deviation of the population, which must also be estimated from the sample. It is sufficient to use the sample estimate of $\sigma$ if the sample is sufficiently large, but if it is not, and small-sample theory must be used, it is to be remembered that small-sample theory assumes that the parent distribution is normal, as in Student's $t$-distribution. It is known that for moderate deviations from normality the $t$ test is valid, but it is now shown that the kurtosis* of the two-strength distribution in its simple or its modified form, may be very pronounced.

The sampling standard error of the standard deviation is given by

$$\sigma_\sigma = \frac{\sigma}{\sqrt{2r}}\left(1 + \frac{\beta_2 - 3}{2}\right)^{\frac{1}{2}} \quad \text{.....(7)}$$

where $\beta_2 = \mu_4/\mu_2^2$ and $\mu_4 = \frac{1}{r}\Sigma(S - \bar{S})^4$

is the fourth moment of the distribution about its mean.

The expression for $\beta_2$ as a function of specimen length for the modified two-strength distribution has been calculated[7] and has a minimum at $l/l_0 = ln2$ and a maximum in each of the ranges $0 < \bar{n} < ln2$, $ln2 < \bar{n} < \infty$. At extreme values of either range it tends to the normal value 3. The position and height of the maxima depend on the values of the standard deviations of the normal components of the distribution, $\sigma_1$ and $\sigma_2$. For the simple two-strength distribution ($\sigma_1 = \sigma_2 = 0$) $\beta_2 = 1$ at $\bar{n} = ln2$, *i.e.*, the sampling error of the standard deviation is zero at this length for the simple model. $\beta_2$, and consequently the sampling error, increases without limit on either side of this value.

The behaviour of $\beta_2$ is shown in Fig. 3 for the range $0 \leqslant n \leqslant 4{\cdot}0$ for the two sets of values: $\sigma_1 = \sigma_2 = 0{\cdot}1(S_1 - S_2)$ and $\sigma_1 = \sigma_2 = 0{\cdot}5(S_1 - S_2)$ at $l/l_0 = 0{\cdot}1$.

The distribution of strengths of chains whose individual links have a normal distribution is also non-normal,[4] but a. the value of $\beta_2$ only increases from 3·06 to 4·09 as the number of links increases from 2 to 1000 the normal approximation may be assumed.

* A population has zero kurtosis if the value of $\beta_2 = \mu_4/\mu_2^2$ is 3.

## EXPERIMENTAL DETERMINATIONS OF EFFECT OF LENGTH OF WIRE ON STRENGTH

The properties of two types of material have been considered in the foregoing sections: a material fairly homogeneous on the scale of the test, the strengths of which show a normal distribution, and one in which there are randomly spaced flaws on this scale. It was decided to investigate the homogeneity of some wire by comparing the results of tensile tests with predictions given by these models.

Tests were accordingly made on specimens cut from straight lengths of phosphor-bronze wire, hard-drawn to $\frac{1}{8}$ in. dia. The tests were carried out on a Hounsfield tensometer; elongation of the specimens was measured by a simple two-mirror extensometer. The tests were carried out as nearly as possible at constant rate of extension. Gauge lengths of $\frac{1}{2}$, 1, 3, 5, 7, 9, and 11 in. were tested, but for the two shorter of these lengths the extensometer could not be used. On these two lengths tensile strength only was measured; on the rest both tensile strength and the permanent elongation at which a neck began to form. The tensile strength was the conventional engineering value of maximum load divided by initial cross-sectional area, but as the strain was quite small in all cases, about 0·01 or less, the value is very nearly equal to the true maximum stress. The plastic 'strain to neck' is taken instead of the usual 'strain to fracture,' which has no simple physical significance; the former is the strain at the end of the period of uniform extension, and is approximately a direct measure of work-hardening.[6]* Twenty specimens of each length were taken, with the following results:

| Specimen Length, in. | Mean Tensile Strength, tons/sq. in. | Mean Strain to Neck | Standard Deviation Tensile Strength, tons/sq. in. | Standard Deviation Strain to Neck |
|---|---|---|---|---|
| 0·5 | 48·8 | ... | 0·98 | ... |
| 1·0 | 47·9 | ... | 1·70 | ... |
| 3·0 | 43·6 | 0·0195 | 5·95 | 0·0040 |
| 5·0 | 43·2 | 0·0077 | 4·80 | 0·0047 |
| 7·0 | 39·9 | 0·0065 | 3·10 | 0·0034 |
| 9·0 | 44·9 | 0·0040 | 4·30 | 0·0009 |
| 11·0 | 39·0 | 0·0037 | 3·50 | 0·0011 |

* The rate of work-hardening during the period of uniform extension must be governed by the weakest part of the test piece, since at any strain in this range the test piece cannot support a greater stress than that corresponding to its weakest cross-section. The plastic 'strain to neck' is therefore determined by a weakest-link criterion.

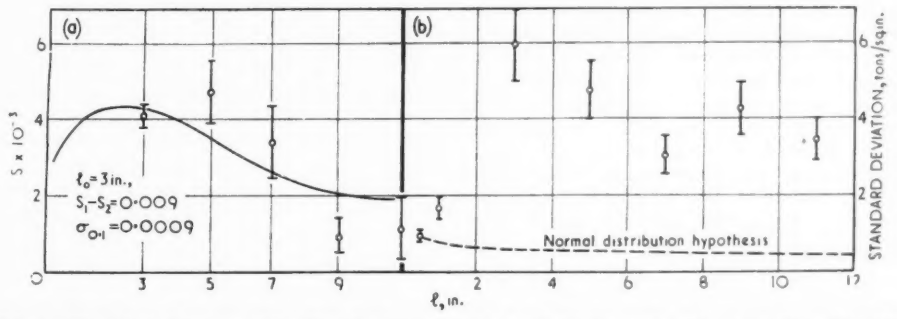


**Fig. 5—Phosphor-bronze wire: Standard error (*a*) of strain to neck, (*b*) of tensile strength**

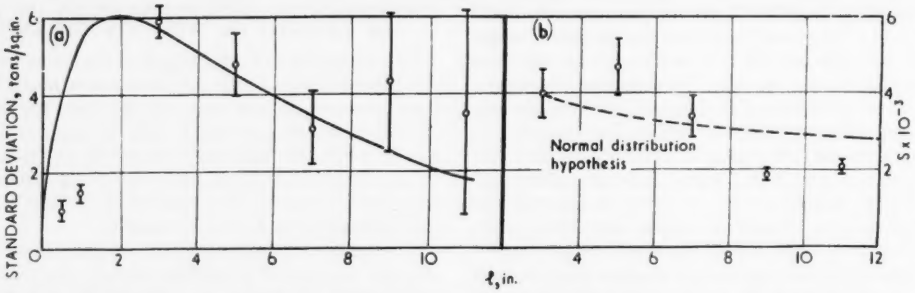


**Fig. 6—Phosphor-bronze wire: Standard error (*a*) of tensile strength, (*b*) of strain to neck**

There appears to be a maximum in the standard deviations at about 3 in., while the means decrease rapidly over the range. The results are plotted in Figs. 4, 5, and 6, together with theoretical curves computed from equation (5) and the square root of equation (6) with the following values for the tensile strength and elongation of flawed and unflawed specimens ($S_1$, $S_2$ and $\varepsilon_1$, $\varepsilon_2$ respectively):

$S_1 = 52{\cdot}5$ tons/sq. in. $\left.\right\}$ $\sigma_{s_1} = \sigma_{s_2} = 1{\cdot}05$ tons/sq. in. at $l/l_0 = 0{\cdot}1$
$S_2 = 42{\cdot}0$ tons/sq. in. $\left.\right\}$

$\epsilon_1 = 0{\cdot}0165$ $\left.\right\}$ $\sigma_{\epsilon 1} = \sigma_{\epsilon 2} = 0{\cdot}0009$ at $l/l_0 = 0{\cdot}1$
$\epsilon_2 = 0{\cdot}0066$ $\left.\right\}$

$l_0 = 3$ in. in both cases.

It appears that these are flaws in the material; it is not possible to determine $l_0$ very accurately from these data, but it is probably between 2 and 5 in.

In Fig. 4 the broken lines show the theoretical variation of the mean, assuming that the distribution of strengths of the shortest length was normal with standard deviation equal to the experimental standard error. In Figs. 5*a* and 6*a* are plotted the standard deviations, together with theoretical curves computed from equation (6), and in Figs. 5*b* and 6*b* the same data with the theoretical curve predicted by the normal-distribution hypothesis. The discrepancy between the two models is especially obvious in Figs. 4*a*, 5*b*, and 6*a* for the tensile strength.

The standard errors which are attached to the means in Fig. 4 are calculated from the formula $S/\sqrt{r}$, where $S$ is the standard error and $r$ the number in the sample. The sampling errors of the standard deviations in Figs. 5*a* and 6*a* are computed from the expression for $\beta_2$ for the two-strength distribution,[7] assuming that the samples were taken from the populations specified above. As was shown in the previous section, errors calculated in this way are sensitive to the values of $\sigma_{S1}$, $\sigma\varepsilon_1$, and $l_0$; but as the given characteristics approximately describe the behaviour of the means the standard deviations of the standard errors are probably of the right order of magnitude, though possibly overestimated by as much as 50% at the end of the range. The standard errors of the standard deviations in Figs. 5*b* and 6*b* are estimated from the formulae for the normal distribution.

## CONCLUSIONS

The effect of length of specimen on the statistical tensile properties of a material have been investigated on the assumption that the test piece behaves like a chain which fails at its weakest link. The variation of mean strength and standard deviation with test length of a material containing randomly spaced flaws, small compared with the specimen size, but the mean distance between which is comparable with the test length, has been compared with the variation for a material which gives a normal distribution of strengths in mechanical tests. Some tests on phosphor-bronze wire have shown that for this metal the former model is appropriate, there being flaws giving rise to low strength and ductility with a mean distance apart of about 3 in.

A consideration of the character of the distribution of strengths of test pieces from a flawed material shows that the sampling techniques appropriate to a normal population, including small-sample methods, may be seriously in error.

It is suggested therefore that the true condition of rod, wire, or strip can only be ascertained by testing different lengths of material, and that the samples for each length should not be small. In practice, not less than three different lengths should be taken, and a sample number of at least 20 for each. However, if these conditions cannot be fulfilled, a rough 'spot check' might be made by testing small samples for a number of lengths. If a defective specimen is defined as being outside some specified strength range, a plot of the natural logarithm of the proportion of non-defective test pieces against length of specimen gives, if the flaws are small and randomly spaced, a straight line whose slope is $1/l_0$.

## APPENDIX

### Averaging Test and Variation of Lateral Dimensions of Specimen

In certain tests the weakest-link theory is not appropriate. For example, instead of the strength of a test piece being that of its weakest point it may represent an average of the measured property throughout the whole specimen, as in the determination of electrical resistivity. Tucker[3] considers that the strength of a test piece represents an average of the strengths over the cross-sectional area, so that in analysing the effect of changing the lateral dimensions of the specimen this model should be used.

Suppose that such a test is being applied to a test piece which we can consider as a number $N$ of parallel elements with a distribution of strengths. The mean strength of a large number of test pieces is the mean of the population of elements, and accordingly inde-

pendent of $N$, *i.e.*, of the lateral dimensions of the test piece. The standard deviation of strengths of specimens, however, is that of the means of samples of $N$, which is $\sigma/\sqrt{N}$, where $\sigma$ is the standard deviation of the distribution of strengths of elements; that is, it is inversely proportional to the square root of the area of cross-section of the test piece, *i.e.*, inversely proportional to the radius, for a round specimen. This is true whatever the character of the distribution of strengths of elements.

Consider a simple two-strength distribution, for example. Let the mean distance between flaws, strength $S_2$, be $2r_0$, and the radius of test piece be $r$.

The mean number of flaws per unit cross-sectional area is:

$$\bar{n} = \frac{\pi r^2}{r_0^2} = \frac{A}{r_0^2}$$

Let the area of a flaw be $A_2$, and $\bar{n}A_2 \ll A$ so that the Poisson law holds for the distribution of flaws.

Let $n$ be the number of flaws in a test piece. The strength of a specimen is then:

$$S = \frac{(A - nA_2)S_1 + nA_2S_2}{A}$$

and the mean strength of a large number of specimens is:

$$\bar{S} = S_1 - \frac{A_2}{A}\bar{n}(S_1 - S_2)$$

$$= S_1 - \frac{A_2}{r_0^2}(S_1 - S_2) \quad \text{.....(i)}$$

The standard deviation of strengths is:

$$\sigma = \frac{1}{r}\sqrt{\Sigma(S_p - \bar{S})^2}$$

where $S_p$ is the strength of the $p$th specimen

$$= \frac{1}{r}\left\{(S_1 - S_2)\frac{A_2}{A}\sqrt{\Sigma(n_p - n)^2}\right\} \text{.....(ii)}$$

Now $\frac{1}{r}\Sigma(n_p - \bar{n})^2$

is the variance of the Poisson distribution and equals $\bar{n}$;

$$\therefore \sigma = \sqrt{\bar{n}}\frac{A_2}{A}(S_1 - S_2) = \frac{A_2}{\sqrt{\pi\{r_0 r(S_1 - S_2)\}}} \text{.....(iii)}$$

Thus the mean is independent of specimen radius, the standard deviation inversely proportional to it.

If the strengths of unit areas of the specimen cross-section are normally distributed with standard deviation $\sigma$, each test piece can be regarded as a sample of $N$ specimens of unit area, and the standard deviations of strengths of test pieces will be the standard deviation of means of samples of $N$, *i.e.*, $\sigma/\sqrt{N}$. Thus the standard deviation is again in this case inversely proportional to the square root of the area of cross-section, *i.e.*, to the specimen radius. This might have been inferred from the fact that $\sigma/\sqrt{N}$ is independent of the character of the parent distribution.

### Acknowledgments

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# The Free Energies of Formation of Tricalcium and Tetracalcium Phosphates

*By J. B. Bookey*

### SYNOPSIS

The reduction equilibria of tricalcium and tetracalcium phosphates with hydrogen have been studied in the temperature range 1250°–1550° C., and the results have been used to calculate the free-energy changes of the following reactions:

$$3CaO(solid) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Ca_3P_2O_8(solid)$$
$$4CaO(solid) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Ca_4P_2O_9(solid)$$
$$P_2(gas) \rightleftharpoons 2[P](1\% \text{ in iron})$$

### Introduction

THE formation of tetracalcium phosphate from lime and from phosphorus and oxygen dissolved in liquid iron was described in a previous paper.[1] To increase our knowledge of phosphorus–oxygen equilibria still further, a study of the free energy of formation of tetracalcium phosphate from lime and from gaseous phosphorus and oxygen was considered to be profitable. The aim of the present work was to determine this last free-energy change and also that

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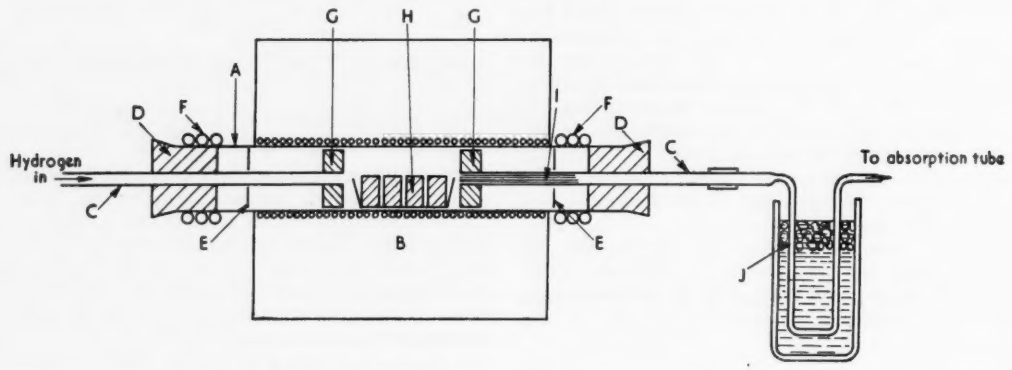


**Fig. 1—Furnace assembly (diagrammatic)**

occurring during the formation of tricalcium phosphate, according to the equations:

$$3CaO(solid) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Ca_3P_2O_8(sol, \alpha) \quad ...(1)$$

$$4CaO(sol) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Ca_4P_2O_9(sol) \quad .....(2)$$

at temperatures in the range 1250°–1550° C.

The experimental method used was to determine two reduction equilibria involving the phosphates, according to the equations:

$$4Ca_3P_2O_8(sol, \alpha) + 5H_2(gas) \rightleftharpoons 3Ca_4P_2O_9(sol) + P_2(gas) + 5H_2O(gas) \quad ...(3)$$

$$Ca_4P_2O_9(sol) + 5H_2(gas) \rightleftharpoons 4CaO(sol) + P_2(gas) + 5H_2O(gas) \quad ...(4)$$

At the temperatures and pressures used, α-tricalcium phosphate (the high-temperature form) containing a little tetracalcium phosphate in solution is in equilibrium with tetracalcium phosphate containing a little tricalcium phosphate, and tetracalcium phosphate containing a little excess lime is in equilibrium with lime.[2, 3] The phosphorus vapour is present almost entirely as $P_2$; the amount of the species $P_4$ is negligible.[4]

The measurements consisted essentially of passing a known volume of hydrogen over the calcium phosphate, contained in a molybdenum boat within an impervious alumina tube, and of the determination of the amount of water in the exit gas, the phosphorus concentration being obtained from the stoichiometry of the reaction.

Two objections can be made to this type of measurement: (*a*) that the gas may not have come to equilibrium with the solid phases, and (*b*) that the slow flow rates often used in the past to minimize objection (*a*) are just those that favour thermal segregation of the gases as they leave the high-temperature region. In this work, these sources of error have been minimized by causing the gas to leave the hot zone through capillaries, in which its high velocity prevented any thermal segregation; also, it was found that the flow rate could be varied over a wide range without affecting the results.

Combination of reactions (3) and (4) gives:

$$Ca_3P_2O_8(sol, \alpha) + 5H_2(gas) \rightleftharpoons 3CaO(sol) + P_2(gas) + 5H_2O(gas) \quad ...(5)$$

and equations (4) and (5) can be combined with the equation

$$2H_2(gas) + O_2(gas) \rightleftharpoons 2H_2O(gas) \quad .....(6)$$

to give equations (1) and (2).

## EXPERIMENTAL DETAILS

### Gas and Train Flowmeter

Cylinder 'oxygen-free' hydrogen was passed successively through tubes of calcium chloride, palladinized asbestos heated to 350° C., Sofnolite, Anhydrone, and phosphorus pentoxide. The pure dry hydrogen then passed through a capillary flowmeter, and the pressure in the apparatus was measured by a mercury manometer at the exit side of the flowmeter. This part of the apparatus was constructed entirely from glass.

The capillary flowmeter was calibrated, by means of a soap-bubble flowmeter, at four different pairs of temperature and pressure. The results agreed well with Poiseuille's equation and were used to calculate the N.T.P. flow rate during experiments; this flow rate is estimated to be within ± 1% of the true value.

### Furnace Assembly

The furnace assembly is shown in Fig. 1. The furnace tube *A* (650 mm. × 30 mm. × 26 mm.) was made of pure recrystallized alumina (Morgan Δ*RR*) and was heated by a platinum-wound furnace *B*. The gas entered and left the hot zone through recrystallized alumina tubes *C*, of 6-mm. bore. These tubes were fitted to the furnace tube by means of well-fitting bungs *D*. Silicone grease helped to make the joints vacuum-tight, and silicone varnish was painted around the outside of the joints. Brass radiation stoppers *E* and water-cooled metal tubing *F* kept the bungs cool. Alundum plugs *G* helped to prevent diffusion of water vapour from the reaction zone to the cooler parts of the tube. Lumps of sintered calcium phosphate were contained in the molybdenum boat *H* in the centre of the furnace. The exit tube was packed with fine alumina tubes *I*, to minimize thermal segregation as the gases left the hot zone. From the exit tube the gases passed through a long **U**-tube *J*, packed in ice, in which almost all the phosphorus vapour was retained, and then through Anhydrone-filled weighing tubes. The partial pressures of water vapour studied were all below the vapour pressure of ice at 0° C., and there was no risk of

condensation of water in the trap. The furnace temperature was controlled to $\pm 3°$ C., by means of a Sunvic energy regulator, and was measured by a Pt/Pt–Rh thermocouple in conjunction with a potentiometer. The thermocouple, which lay along the outside of the furnace tube, was guaranteed to $\pm 3°$ C. at 1500° C., and this was accepted without further calibration; at 1500° C. the temperature distribution along the centre 2 in. of the furnace was not more than $\pm 3°$ C.

### Calcium Phosphate Container

In a preliminary experiment, tricalcium phosphate was rammed into the centre of the furnace tube and held there between two Alundum plugs. It was hoped that the gas would pass through the phosphate, giving itself every chance to come to equilibrium with the solids. After hydrogen had been passed through the heated furnace for some days, the tube was cooled and the phosphate plug removed. It was found that the phosphate had reacted with the alumina tube and had partially melted, but the reaction had taken place only in the vicinity of the leading face of the plug. The phosphate had also shrunk a little, allowing the gas ready passage between it and the tube. Neither tricalcium nor tetracalcium phosphates react with sintered alumina in air at 1500° C., and these observations therefore seem to indicate that the reaction was so fast that the gas, after it had passed the first centimetre of the surface of the plug, was substantially in equilibrium with the phosphate. This reaction with the furnace tube was probably due to the formation of calcium aluminate instead of tetracalcium phosphate, with the lime at a lower potential. The equilibrium water-pressure determined at the first temperature studied was the same as that for the true reduction to tetracalcium phosphate, but in subsequent determinations higher water-pressure values were found.

These results necessitated a search for a crucible material resistant at high temperatures to hydrogen, alumina, lime, calcium phosphates, and phosphorus vapour. Previous work suggested that molybdenum might fulfil these conditions. Accordingly, 4 g. of molybdenum sheet were formed into a boat and heated for 60 hr. at 1400° C. in a stream of hydrogen containing about 0·5 mm. partial pressure of phosphorus vapour. After this time the boat had not changed in appearance but was very brittle; it contained 8% of phosphorus. Such a phosphided molybdenum boat was found to be suitable and was used for the tricalcium and tetracalcium phosphate reductions. At the end of the latter it was found to contain 10·0% of phosphorus ($Mo_{2\cdot9}P$, *cf.* $Mo_3P$).

### Materials Used

The preparation of the tetracalcium phosphate used in this work has been described previously.[1] The β-tricalcium phosphate was similarly prepared, and could be transformed into the α form by ignition for 3 hr. at 1500° C. Both forms of the tricalcium phosphate were identified by means of their X-ray diffraction patterns. To each phosphate was added a 2% excess of lime, to ensure that the initial furnace charges consisted of the two equilibrium phases, and the mixtures were ignited in air for 6 hr. at 1500° C. just before use.

### Procedure

The apparatus was initially assembled without any boat or charge, and was tested for leaks. When found to be gas-tight the furnace was heated to 1450° C., with hydrogen passing through the tube. After 24 hr. the pressure of water vapour in the exit gas had dropped to 0·075 mm., which was considered to be satisfactory. The furnace was cooled, the boat containing porous lumps of calcium phosphate inserted, the system made gas-tight, and the furnace reheated to 1400° C. and left for 60 hr. with a slow stream of hydrogen passing. During this period, and from then onwards, ice was maintained around the phosphorus trap; at the end of this period the hydrogen flow rate was increased to about 2 litres/hr. and the bubbler at the end of the trap was replaced by an Anhydrone-filled absorption tube and a guard tube, which were left to absorb the water coming from the furnace. During the time that these tubes were connected, the flow rate and furnace temperature were kept steady, the barometer was read and the temperature of the flow meter capillary noted. At the end of a definite time the tubes were disconnected and the absorption tube was reweighed. The partial pressure of water in the gas stream was then calculated from these measurements, which were repeated until concordant results were obtained. Other determinations were carried out at various flow rates and temperatures, with the same sample still in the furnace.

When the system had been left overnight in a slow stream of hydrogen, the first determinations of the water-vapour pressure gave varying results. This was presumably due to the enhanced effects of small leaks at low flow rates, and to some thermal diffusion of water vapour past the Alundum plugs into the cold part of the furnace tube. When the hydrogen flow rate was increased, the conditions in the stagnant parts of the system were disturbed and erratic results prevailed until the system was again steady.

Measurements were made with tricalcium phosphate at 50° C. intervals from 1250° to 1500° C. When measurements were attempted at 1550° C., low results were obtained; analysis of the phosphate when the furnace had cooled showed that the mixture contained only 41·5% of $P_2O_5$, *i.e.*, that the tricalcium phosphate had been reduced almost entirely to tetracalcium phosphate (39% $P_2O_5$).

Measurements were made on the tetracalcium phosphate at nine temperatures in the range 1300°–1550° C. In addition, a fresh charge of tetracalcium phosphate was inserted in the furnace and measurements were made **at** one temperature, 1450° C. The resultant water-vapour pressure was 1·23 mm., which compares well with the value 1·21 mm. obtained in the main series of experiments. The temperature sequence of runs was not systematic.

At the end of each of the two main series of experiments, the Anhydrone in the weighing tube was analysed for entrapped phosphorus. Small amounts were found, equivalent to about 75% of the phosphorus vapour pressure at 0° C. (the temperature in the trap). Weights of phosphorus proportional to

**Table I**

**REDUCTION OF CALCIUM PHOSPHATES**

| Temperature, °C. | $P_{H_2O}$, mm. | $\log_{10}K$ |
|---|---|---|
| **Reduction of $Ca_3P_2O_8$** | | |
| 1250 | 0·49 | −19·84 |
| 1300 | 0·73 | −18·79 |
| 1350 | 1·03 | −17·91 |
| 1400 | 1·36 | −17·20 |
| 1450 | 1·93 | −16·27 |
| 1500 | 2·79 | −15·32 |
| **Reduction of $Ca_4P_2O_9$** | | |
| 1300 | 0·43 | −20·17 |
| 1350 | 0·61 | −19·32 |
| 1400 | 0·84 | −18·44 |
| 1425 | 1·11 | −17·70 |
| 1450 | 1·21 | −17·48 |
| 1475 | 1·55 | −16·86 |
| 1500 | 1·78 | −16·51 |
| 1525 | 2·07 | −16·10 |
| 1550 | 2·55 | −15·55 |

the volume of hydrogen passed were subtracted from the weights of water found during runs; this small correction affected only the results at low water pressures.

The error in the determination of the water-vapour pressure is estimated to be not more than ± 7% of the true value.

The products of the reductions were analysed for their $P_2O_5$ content and examined by X-ray diffraction. The 'tricalcium phosphate' (41·5% $P_2O_5$) showed diffraction lines of both phosphates. The 'tetracalcium phosphate' (30·9% $P_2O_5$) showed diffraction lines of both this phosphate and lime.

## RESULTS

For the reduction of the tricalcium phosphate, the standard deviation of the mean of the several values at each temperature was always less than 2·5%; for the tetracalcium phosphate it was less than 1·5%. There was no significant variation of the results with flow rate. In the reduction of tricalcium phosphate at 1300°C., for instance, the flow rate was varied threefold, but the water pressures obtained (flow rate increasing successively) were 0·70, 0·73, 0·77, 0·72, and 0·74 mm.

A total of 70 runs was made. From the several results at each temperature, the average equilibrium values of the water-vapour pressure were obtained (*see* Table I), and the equilibrium constants of the reactions at each temperature were then derived as follows:

For reaction (3), the equilibrium constant $K_3$* is given by

$$K_3 = p_{H_2O}{}^5 \times p_{P_2}/p_{H_2}{}^5,$$

where $p_{H_2O}$, $p_{P_2}$, and $p_{H_2}$ refer to the partial pressures (in mm.) of the three species.

From the stoichiometry of the reaction

$$p_{P_2} = p_{H_2O}/5,$$

and if $P_{tot}$ is the total pressure in the apparatus,

$$p_{H_2} = P_{tot} - (p_{H_2O} + p_{P_2}) = P_{tot} - 6p_{H_2O}/5$$

Hence $K_3 = p_{H_2O}{}^6/5(P_{tot} - 6p_{H_2O}/5)^5$

or $K_3(\text{atm.}) = p_{H_2O}{}^6/5 \times 760(P_{tot} - 6p_{H_2O}/5)^5$.

For reaction (4) the same reasoning can be applied, and $K_4$ is given by an expression similar to that for $K_3$. Table I gives also the calculated values of $\log_{10}K_3$ and $\log_{10}K_4$.

### Interpretation of the Data

The variation of an equilibrium constant with temperature is given by the equation:

$$\frac{\partial \log_e K_p}{\partial(1/T)} = \frac{\Delta H^\circ}{R},$$

where $T$ is the temperature, in ° K., and $\Delta H^\circ$ is the standard heat of reaction.

When the results in Table I are plotted as graphs of $\log_{10}K$ against $1/T$, as in Fig. 2, the points lie on a straight line, within the accuracy of the experiments, and can well be represented by the equations:

$$\log_{10}K_3 = 12·85 - \frac{50{,}000}{T}$$

$$\log_{10}K_4 = 13·94 - \frac{53{,}850}{T}.$$

These can be converted to free-energy expressions by means of the relationship $-\Delta G^\circ = 2·303RT\log_{10}K$. The resulting equations are:

$$\Delta G^\circ{}_3 = 228·8 - 0·0588T \text{ kg.cal.}$$
$$\Delta G^\circ{}_4 = 246·4 - 0·0638T \text{ kg.cal.},$$

and taking $(\Delta G^\circ{}_3 + 3\Delta G^\circ{}_4)/4$ gives:

$$\Delta G^\circ{}_5 = 242·0 - 0·0625T \text{ kg.cal.}$$

In these equations, the first terms can be identified with the heats of reaction $\Delta H^\circ$, and the negative coefficients of $T$ can be identified with the standard entropy changes ($\Delta S^\circ$) of the reactions, all values being the average over the temperature range considered. In practice, these quantities do not vary greatly with temperature.

Richardson and Jeffes[5] have shown that the data for reaction (6), the formation of water from its elements, can adequately be represented by

$$\Delta G^\circ{}_6 = -118·0 + 0·02675T \text{ kg.cal.},$$

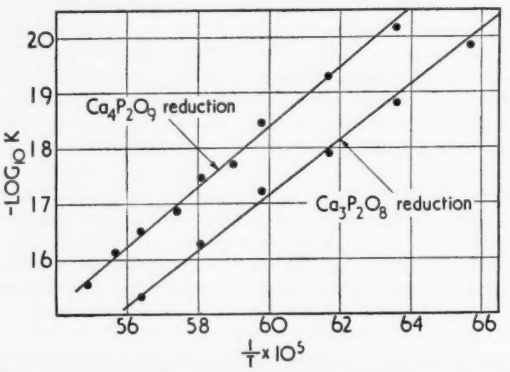


**Fig. 2—Plot of $\log_{10}$ (equilibrium constant) against reciprocal temperature**

* Subscripts to $K$ and $\Delta G$ refer to the number of the equation describing the relevant reaction.

and suitable combination of this with $\Delta G^\circ_4$ and $\Delta G^\circ_5$ gives the free energies of formation of the two phosphates from lime, phosphorus, and oxygen.

$\Delta G^\circ_1$ (tricalcium phosphate)
$= -537{\cdot}0 + 0{\cdot}1294T \pm 3$ kg.cal.

$\Delta G^\circ_2$ (tetracalcium phosphate)
$= -541{\cdot}4 + 0{\cdot}1307T \pm 2$ kg.cal.

The above error limits were ascribed after due consideration of the various errors involved, as already mentioned.

## DISCUSSION

The amount of water found in the exit gas, 0·075 mm. partial pressure, when dry hydrogen was passed through the hot tube, calls for some comment. Part of this was due to desorption of water from the refractories (which is known to be a slow process), but some part was doubtless due to small leaks and to diffusion of oxygen through the hot walls of the refractory tube. The water pressures measured in the course of this work were of the order of 1 mm., of which 0·075 mm. is 7·5%, but this water-vapour pressure would not cause a 7·5% error in the measured values, as its presence in the hot zone would prevent, to some extent, the reduction reaction. It can be calculated that in these circumstances the measured water-vapour pressure would be only 2·5% high. This was taken into account when the possible total error in the water-vapour pressure measurements was put at 7%. The 0·075 mm. pressure of water vapour compares well with the experience of other workers.[6]

Franck and Füldner[7] have studied reactions involving tricalcium phosphate, calcium phosphide, lime, and carbon, as solid phases. From their graphs of the phosphorus and carbon monoxide pressures developed when these mixtures were heated, the free-energy change of the reaction

$$Ca_3P_2O_8(sol) + 5C(sol) \rightleftharpoons 3CaO(sol) + P_2(gas) + 5CO(gas)$$

and hence of reaction (1) has been calculated by the present author to be:

$\Delta G^\circ_1$ (Franck and Füldner) $= -678{\cdot}0 + 0{\cdot}300T$ kg.cal.

This value is greatly different from that obtained in the present work, but the assumptions made by Franck and Füldner about the rôle of calcium phosphide in the above reaction are questionable.

Thermal data provide a comparison with the present work. The heats of the following reactions have been determined, in this laboratory,[8] by solution calorimetry:

$$3CaO(sol) + P_2O_5(sol, H) = Ca_3P_2O_8(sol, \alpha \text{ or } \beta)$$
$$\Delta H^\circ_{298} = -161{\cdot}95 \pm 3 \text{ kg.cal.}$$
$$4CaO(sol) + P_2O_5(sol, H) = Ca_4P_2O_9(sol)$$
$$\Delta H^\circ_{298} = -172{\cdot}36 \pm 3 \text{ kg.cal.}$$

(The phosphorus pentoxide used in these experiments had been sublimed *in vacuo* and was in the hexagonal form.[9, 10]) These heats of formation were combined with the heat of formation of phosphorus pentoxide,[11] $P_2$ gas,[12] and the specific heats[13] of calcium oxide, $P_2$ gas, oxygen, and tricalcium phosphate, to give the free-energy change of reaction (1) at temperatures in the range 298°–1600° K. The results were plotted and a straight line was drawn through the points. Tricalcium phosphate undergoes a transition at 1373° K., but the break in the $\Delta G/T$ line is small, and little error is introduced when the results are presented as

$\Delta G^\circ_1$(thermal) $= -541{\cdot}1 + 0{\cdot}1369T \pm 20$ kg.cal.

Assuming that the entropy change of the reaction

$$CaO(sol) + Ca_3P_2O_8(sol) = Ca_4P_2O_9(sol)$$

is zero, the standard free-energy change of reaction (2) can be calculated to be

$\Delta G^\circ_2$ (thermal) $= -551{\cdot}5 + 0{\cdot}1369T \pm 20$ kg.cal.

These equations agree well with the high-temperature equilibrium data. A comparison of the results obtained from the two equations, thermal and experimental, is given in Table II.

**Table II**

**STANDARD FREE-ENERGY CHANGES (kg.cal.) FOR REACTIONS (1) AND (2)**

| Method | $\Delta G^\circ_1$ | | $\Delta G^\circ_2$ | |
|---|---|---|---|---|
| | 300° K. | 1600° K. | 300° K. | 1600° K. |
| Experimental | −498·2 | −330·0 | −502·2 | −332·3 |
| Thermal | −500·0 | −322·0 | −510·4 | −332·4 |

The results for reaction (4) can be combined with those of Bookey, Richardson, and Welch[1] for the reaction*

$$4CaO(sol) + 2[P](1\% \text{ concn.}) + 5H_2O(gas) \rightleftharpoons Ca_4P_2O_9(sol) + 5H_2(gas)$$

to give the free-energy change for the solution of $P_2$ gas in liquid iron:

$$P_2(gas) = 2[P](1\% \text{ concn.}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$
$$\Delta G^\circ_7 = -58{\cdot}5 - 0{\cdot}0091T \pm 2{\cdot}5 \text{ kg.cal.}$$

This uncertainty limit applies to the free-energy change; the uncertainty in the individual heat and entropy terms is considerably greater.

The above value of the free-energy change of the solution of phosphorus in liquid iron differs somewhat from the very rough estimate of Richardson and Jeffes,[14] *i.e.*,

$\Delta G^\circ_7$ (Richardson and Jeffes) $= -101{\cdot}6 + 0{\cdot}0066T \pm 20$ kg.cal.,

although at 1550° C. the difference between the two is well within the estimated uncertainty limits.

## Acknowledgment

The author wishes to thank Dr. J. Pearson and Dr. E. T. Turkdogan, both of the Chemistry Department of the British Iron and Steel Research Association, for many helpful discussions.

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* Square brackets denote solution in liquid iron.

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# The Free Energy of Formation of Magnesium Phosphate

*By J. B. Bookey*

**SYNOPSIS**

The reduction equilibrium of magnesium orthophosphate with hydrogen has been studied in the temperature range 1000°–1250° C., and the results are used to calculate the free-energy change of the reaction

$$3MgO(solid) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Mg_3P_2O_8(solid).$$

## Introduction

DESPITE numerous investigations of the equilibria between liquid iron, containing phosphorus, and slags of various complex constitutions, the relative rôles of lime and magnesia in effecting dephosphorization are still not clear. In the work of Schenck[1] and of Balajiva, Quarrell, and Vajragupta,[2] for instance, magnesia was regarded as an inert diluent, whereas Winkler and Chipman[3] regarded lime, magnesia, and manganous oxide as being equivalent.

The present determination of the free energy of formation of magnesium phosphate has been carried out as a continuation of the previous work on pure calcium phosphate systems, and as a preliminary to studies in this laboratory, on complex dephosphorizing slags.[4, 5] The experimental method used was essentially that of the previous investigation[4] (*see* p. 61) of the free energies of formation of tricalcium and tetracalcium phosphates, and will not be described in detail. Briefly, the reduction equilibrium of magnesium phosphate and hydrogen, according to the equation

$$Mg_3P_2O_8(solid) + 5H_2(gas) \rightleftharpoons 3MgO(sol) + P_2(gas) + 5H_2O(gas) \ldots (1)$$

was measured by passing hydrogen over heated magnesium phosphate and determining the concentration of water in the exit gas, the phosphorus concentration being obtained from the stoichiometry of the reaction. Suitable combination of the free-energy change for reaction (1) with that for the reaction

$$2H_2(gas) + O_2(gas) \rightleftharpoons 2H_2O(gas) \ldots\ldots\ldots\ldots (2)$$

gives the required information for reaction (3):

$$3MgO(sol) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Mg_3P_2O_8(sol) \ldots (3)$$

At the temperatures and pressures used, gaseous phosphorus is present almost entirely as $P_2$ molecules.[6]

### THE $MgO$–$P_2O_5$ SYSTEM

The experimental method involves the assumption that the MgO and $Mg_3P_2O_8$ are present as pure solid phases in equilibrium with each other at the temperatures of the experiments. A study of the literature revealed little information on this subject, and before the reduction equilibrium measurements could be started it was necessary first to clarify the phase relationships at the basic end of the $MgO$–$P_2O_5$ system.

X-ray diffraction and cooling-curve analyses were carried out on samples of various compositions between $Mg_3P_2O_8$ and MgO. These samples were prepared by mixing suitable proportions of AnalaR magnesium oxide and diammonium phosphate and heating the mixture, contained in a platinum crucible, slowly to 1000° C. The weight losses agreed closely with those calculated from the equation:

$$3MgO + 2(NH_4)_2.HPO_4 = Mg_3P_2O_8 + 4NH_3 + 3H_2O.$$

Small samples were ignited in air at 1000° and 1250° C. for several hours, quickly cooled, and then submitted to X-ray diffraction analysis.

The results of this work, given in Table I, show that there are no fresh phases, such as $Mg_4P_2O_9$ (*cf.*

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$Ca_4P_2O_9$), between $Mg_3P_2O_8$ and MgO. The low sensitivity of the method does not preclude the existence of some solid solubility between these two phases, but if such a solubility exists at all it would probably not be large. These results are in accord with the limited work of Klement.[7]

Cooling curves were taken by means of a bare Pt/Pt–Rh thermocouple immersed in the $MgO–P_2O_5$ melt, which was contained in a platinum crucible within a platinum-wound furnace. The atmosphere was air. The melting point of pure $Mg_3P_2O_8$ was found to be $1430 \pm 5°$ C., and the $Mg_3P_2O_8$–MgO eutectic temperature, determined with compositions $4MgO,P_2O_5$ and $4{\cdot}6MgO,P_2O_5$, was found to be $1330 \pm 5°$ C. At the end of these determinations the melt was sampled with a cold copper rod, and the result of X-ray diffraction analysis of this sample is also given in Table I.

## EXPERIMENTAL DETAILS

The apparatus used in the previous study of calcium phosphates was very satisfactory, and only minor modifications were made for the present work. The two highest water pressures measured exceeded the vapour pressure of ice, and to prevent condensation of water the ice around the phosphorus trap was replaced during these runs by water at 10° C.

Preliminary experiments showed that when measurements of the equilibrium water-vapour pressure had been made at several temperatures and then repeated at the first temperature of the series, consistent results were not obtained. It was suspected that these aberrations were due to the slowness of the molybdenum boat in attaining equilibrium with the phosphorus content of the gas, and in the main series of experiments the molybdenum boat was replaced by one of recrystallized alumina ($\Delta RR$). This was possible because magnesia, unlike lime, does not attack alumina in the temperature range 1000°–1250° C. This modification eliminated the irregular results, and all the equilibrium measurements quoted in this paper were obtained using an alumina boat.

These irregularities were not found in the calcium phosphate work, presumably because the higher temperatures and lower phosphorus pressures enabled the molybdenum to equilibrate more quickly.

The initial runs, at 1100° C., were made on a material of composition $4MgO,P_2O_5$, and gave a water-vapour pressure of 2·04 mm.; the final measurements were a redetermination at this temperature, and gave a pressure of 2·02 mm. The temperature sequence of runs was not systematic.

The results obtained at 1150° C. showed the constancy of the equilibrium water-vapour pressure even with a three-fold variation of flow rate.

In equilibrium studies it is desirable, if possible, to demonstrate the reversibility of the reaction by an approach to equilibrium from both sides. In the present work this would be possible only if phosphorus and water vapours and hydrogen could be passed over magnesia and their concentrations determined in the exit gas, which is not an easy task. However, an approach was made to this all-important criterion of reversibility by carrying out reductions with hydrogen containing a small amount of water vapour. An all-glass **U**-tube, each limb measuring 25 cm. × 3 cm., filled with a mixture of hydrated and anhydrous oxalic acid, was sealed between the gas purification and metering train and the furnace. Two 3-way taps and a by-pass allowed the hydrogen to pass on dry or to enter the furnace containing a partial pressure of water vapour equal to that of the $H_2C_2O_4,2H_2O–H_2C_2O_4$ system at the temperature of the water bath in which the **U**-tube was immersed. The variation of this dissociation pressure with temperature has been studied by Baxter and Lansing,[8] and by the author and N. C. Tombs[9] (*see* p. 86), and is known with some certainty.

In the reduction runs, at 1100° C., in which moist hydrogen was used, the pressure of water vapour in the inlet gas was 1·25 mm. and that in the exit gas was 2·18 mm. A value of 2·03 mm. was obtained when dry hydrogen was used.

After removal from the furnace at the end of the experiments, the magnesium phosphate was analysed to be $13{\cdot}4\ MgO,P_2O_5$ and showed no sign of reaction with the boat. X-ray diffraction analysis indicated the presence of $Mg_3P_2O_8$ and MgO.

**Table I**

**X-RAY DIFFRACTION RESULTS**

| Composition | Treatment | Phases Found |
|---|---|---|
| $Mg_3P_2O_8$ | 1000° C. | $Mg_3P_2O_8$ |
| $Mg_3P_2O_8$ | 1250° C. | $Mg_3P_2O_8$ |
| $Mg_3P_2O_8$ | From melt | $Mg_3P_2O_8$ |
| $4MgO,P_2O_5$ | 1000° C. | $Mg_3P_2O_8$ |
| $4{\cdot}6\ MgO,P_2O_5$ | From melt | $Mg_3P_2O_8$ + MgO |
| $6MgO,P_2O_5$ | 1000° C. | $Mg_3P_2O_8$ + MgO |
| $6MgO,P_2O_5$ | 1250° C. | $Mg_3P_2O_8$ + MgO |
| $13{\cdot}4\ MgO,P_2O_5$ | After runs | $Mg_3P_2O_8$ + MgO |

**Table II**

**REDUCTION OF MAGNESIUM PHOSPHATE**

| Temperature, ° C. | $P_{H_2O}$, mm. | $\log_{10}K_1$ |
|---|---|---|
| **Reduction with dry hydrogen** | | |
| 1000 | 0·82 | −18·50 |
| 1025 | 1·03 | −17·89 |
| 1050 | 1·29 | −17·34 |
| 1100 | 2·04 | First determination |
| 1100 | 2·03 | −16·11 |
| 1100 | 2·02 | Last determination |
| 1150 | 3·08 | −15·05 |
| 1200 | 4·33 | −14·09 |
| 1250 | 5·84 | −13·29 |
| **Reduction with moist hydrogen (inlet water pressure 1·25 mm.)** | | |
| 1100 | 2·18 | −16·31 |

## RESULTS

The results of 54 runs are summarized in Table II. The standard deviation of the mean of the several values at each temperature was always less than 3%.

The equilibrium constant of reaction (1) was calculated, as in the previous paper, from the equation

$$K_1(\text{atm.}) = p_{H_2O}{}^6/5 \times 760(P_{tot} - 6p_{H_2O}/5)^5$$

where $p_{H_2O}$ is the equilibrium water-vapour pressure

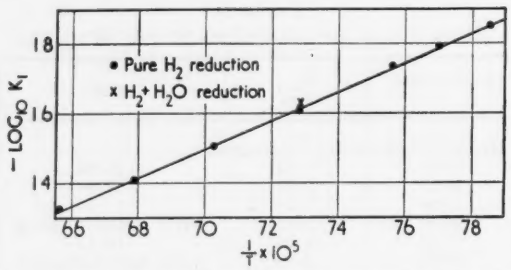


**Fig. 1—Plot of $\log_{10}$(equilibrium constant) against reciprocal temperature**

and $P_{tot}$ is the total pressure in the furnace, both in mm. For the runs in moist hydrogen, if $p_{ox}$ is the inlet partial pressure of water vapour from the oxalic acid hydrate, then the partial pressure $p_{P_2}$ of phosphorus in the exit gas is given by

$$p_{P_2} = (p_{H_2O} - p_{ox})/5.$$

Hence

$$K_1(\text{atm.}) = p_{H_2O}{}^5(p_{H_2O} - p_{ox})/5 \times 760(P_{tot} - 6p_{H_2O}/5 + p_{ox}./5)^8.$$

If the results shown in Table II are plotted as a graph of $\log_{10}K_1$ against $1/T$, as in Fig. 1, they can well be represented by the straight line

$$\log_{10}K_1 = 13{\cdot}75 - \frac{41{,}100}{T},$$

which on conversion to a free-energy expression by means of the relationship

$$-\Delta G^\circ = 2{\cdot}303\ RT\log_{10}K$$

becomes $\Delta G^\circ_1 = 188{\cdot}0 - 0{\cdot}0629T$ kg.cal.

Taking Richardson and Jeffes'[10] value of the free-energy change for reaction (2),

$$\Delta G^\circ_2 = -118{\cdot}0 + 0{\cdot}02675T \text{ kg.cal.},$$

suitable combination with $\Delta G^\circ_1$ gives the free energy of formation of magnesium phosphate from magnesia, phosphorus, and oxygen:

$$\Delta G^\circ_3 = -483{\cdot}0 + 0{\cdot}1298T \pm 1{\cdot}5 \text{ kg.cal.}$$

The uncertainty limit was derived from a consideration of the various sources of error, as in the previous paper.

## DISCUSSION

As can be seen from Fig. 1, the result for the reduction with moist hydrogen falls close to the line representing the reduction with dry hydrogen; this supports the assumption that the reaction studied is reversible.

There is little published information with which these results can be compared. The best that can be done is to inspect them in the light of the results obtained for tricalcium phosphate[4] (*see* p. 64):

$$3CaO(sol) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Ca_3P_2O_8(sol) \ldots (4)$$
$$\Delta G^\circ_4 = -537{\cdot}0 + 0{\cdot}1294T \text{ kg.cal.}$$

The above results agree well with thermal data, and provide a firm reference point.

The entropy terms in the expressions for $\Delta G^\circ_3$ and $\Delta G^\circ_4$ are almost identical, as is to be expected for two similar reactions. The difference in the heat terms is 54·0 kg.cal., and this can be compared with the calorimetrically determined difference.

Berthelot[11] determined the heat change of the reaction

$$3MgO + P_2O_5 = Mg_3P_2O_8 \quad \Delta H^\circ_{298} = -114{\cdot}9 \text{ kg.cal.}$$

and Jeffes[12] determined that of the corresponding reaction of lime:

$$3CaO + P_2O_5 = Ca_3P_2O_8 \quad \Delta H^\circ_{298} = -162{\cdot}0 \text{ kg.cal.}$$

In this case, the difference in the heat terms is 47·1 kg.cal., which is not greatly different from the figure determined from equilibrium data given above. A calorimetric redetermination of the heat of formation of magnesium phosphate is planned in this laboratory.

From a consideration of the results presented in this and the previous papers in the series, a semi-quantitative answer can now be given to the question whether magnesia can play any rôle in the dephosphorization reaction in basic steelmaking. From the free-energy changes of the reactions

$$4CaO(sol) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Ca_4P_2O_9(sol)$$

and

$$3MgO(sol) + P_2(gas) + 2\tfrac{1}{2}O_2(gas) \rightleftharpoons Mg_3P_2O_8(sol) \ldots (3)$$

it can be shown that at steelmaking temperatures* the ratio of the equilibrium phosphorus concentrations in iron, $[P]_{Ca}/[P]_{Mg}$, for the pairs $Ca_4P_2O_9$–CaO and $Mg_3P_2O_8$–MgO is $4 \times 10^{-4}$, approximately independent of oxygen concentration. It is difficult to say precisely what would be the effect on this ratio when the phosphates are present as basic slag components, but it does seem fairly certain from these figures that magnesia has a negligible effect, compared with lime, in dephosphorization; this agrees with basic steelmaking experience.

## Acknowledgment

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* The data for the solid $Mg_3P_2O_8$–MgO system have been extrapolated above the eutectic temperature.

# Thermodynamic Properties of Silicon Monoxide

## AN EXPERIMENTAL STUDY OF THE EQUILIBRIA $SiO_2 + Si \rightleftharpoons 2SiO$ AND $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$

*By N. C. Tombs, Ph.D., A.R.C.S., D.I.C., and A. J. E. Welch, Ph.D., A.R.C.S., D.I.C.*

**SYNOPSIS**

An inert-gas entrainment technique has been used to measure equilibrium pressures of gaseous silicon monoxide (formed in the reversible reaction $SiO_2 + Si \rightleftharpoons 2SiO$) over mixtures of silica and silicon, at 1200°–1650° C. The results are used to compute standard free-energy changes for formation of gaseous silicon monoxide from silica and silicon over this temperature range. A flow method involving rapid cooling of the equilibrium gas atmosphere (to prevent reversal of the reaction) has been used to obtain equilibrium constants and standard free-energy data for the reaction $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$, at 1200°–1650° C. Data for the two reactions are correlated and compared with results of previous measurements. The significance of the results in steelmaking practice is briefly considered.

### Introduction

THE existence of a relatively unstable gaseous monoxide of silicon has long been recognized, the first traceable reference to such a substance being by Winkler.[1] Early in the present century the technical and patent literature contained a number of references to a voluminous condensate, usually brown in colour, obtained by reduction of silica[2]; this product was marketed under the trade name Monox, and various industrial uses were proposed for it. Monox was regarded as a very finely divided mixture of silicon and silica, formed by decomposition of a monoxide of silicon which was stable only in the gaseous state at high temperatures; this interpretation of the constitution of the solid material received some confirmation by later X-ray examination,[3] but probably does not apply under all conditions of preparation. More recent work[4–6] has repeatedly confirmed that mixtures of silicon and silica readily volatilize in a vacuum at temperatures such that independent sublimation of the components cannot occur to an appreciable extent. The brown condensate always approximates to SiO in net composition, and is regarded as a ' disproportionation ' product of gaseous silicon monoxide formed by the reversible reaction $Si + SiO_2 \rightleftharpoons 2SiO$. The work of Zintl *et al.*[5] has consolidated these conclusions and clarified the principal features of the chemistry of silicon monoxide. These investigators have also shown that silica combined in certain refractory silicates (*e.g.*, beryl and zircon) can be removed completely, as gaseous silicon monoxide, by heating the silicate in a vacuum at 1450° C. with the requisite quantity of silicon.[5]

The use of siliceous refractories at high temperatures under reducing conditions is common practice, and there are many oxidation–reduction processes involving siliceous slags. Considerable interest, therefore, attaches to the properties of silicon monoxide and to its participation in processes involving the reduction of silica or silicates. This paper deals with the thermodynamic properties of gaseous silicon monoxide, and a subsequent paper will indicate how the iron–silicon–oxygen equilibria at steelmaking temperatures can be formally treated by assuming that silicon monoxide occurs as an intermediate stage in the reduction of silica to silicon. This assumption has already been postulated by Zapffe and Sims,[7] who have reviewed their work from the viewpoint of the practical steelmaker.[4] Zapffe[8] has also considered the chemistry of silicon monoxide and other volatile ' suboxides ' in connection with ceramic technology.

The thermodynamic properties of silicon monoxide have already been studied by several investigators, but the results are widely discordant. The heat of formation of the dark-coloured vitreous ' silicon monoxide ' of uncertain constitution, obtained by condensing the gas under defined conditions, has been determined to be $103 \pm 3$ kg.cal.[9] or 101·4 kg.cal.[10] per g.mol. of SiO, at normal temperatures. An entrainment method has been used[11] to obtain values of the equilibrium constant (at 1200°–1500° C.) of the reaction $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$, from which the values of standard free-energy change and other thermodynamic functions may be computed. Two groups of investigators[6, 12–14] have used effusion methods to determine the equilibrium pressures of silicon monoxide over mixtures of silicon and silica in the temperature range 900°–1200° C., from which the standard free-energy changes for the reaction $SiO_2 + Si \rightleftharpoons 2SiO$ may be calculated. These studies should suffice to establish the principal thermodynamic properties of gaseous silicon monoxide, but

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unfortunately the results disagree too widely to be of practical value; they are further discussed below.

## PRELIMINARY STUDY OF FORMATION OF SILICON MONOXIDE

Fairly rapid volatilization of mixtures of silica and silicon on heating in a vacuum at 1300° C. was confirmed by preliminary experiments, in which the characteristic brownish condensate reported previously was always obtained. In a few experiments the evacuated furnace tube contained a 'liner,' comprising a slightly smaller refractory tube cut in half longitudinally; after an experiment the liner was removed and the halves separated so that the condensate could be carefully examined and collected. These experiments showed that the condensate was never homogeneous, but varied in character from a light-brown 'fluffy' mass to an almost black vitreous material adhering much more closely to the condensing surface. Analyses of different portions of a typical batch of the condensate showed that they all approximated in composition to the empirical formula SiO, but that definite variations of the silicon/oxygen ratio occurred in different parts of the deposit. Some of the specimens, particularly those of the black vitreous type, were amorphous to X-rays; others gave powder photographs containing a few diffuse lines attributed to silicon and silica. Weighing and analysis of the reacting mixture of silica and silicon, before and after a series of experiments, confirmed the loss by volatilization of material of net composition SiO.

These observations indicate clearly that the condensation of silicon monoxide is a complex process, and that products of widely different character may be obtained under different conditions. This conclusion may explain apparently divergent observations on the constitution of condensed 'silicon monoxide'; thus, Baumann[3] regards the material as a mixture of silica and silicon, whereas Grube and Speidel[15] give X-ray evidence of the existence of an amorphous solid form of silicon monoxide in the black, vitreous condensates. The observations outlined above are in good agreement with those of Grube and Speidel.

A commercial sample of solid 'silicon monoxide,' obtained from the United States and believed to have been prepared by very rapid chilling of the gas from a high temperature, was similar in properties to the vitreous material already described, and gave a similar X-ray pattern. This solid probably corresponds with the amorphous solid of Grube and Speidel.

More detailed accounts of these preliminary experiments have been given elsewhere.[16]

## THE EQUILIBRIUM $SiO_2 + Si \rightleftharpoons 2SiO$

### The Entrainment Technique

If a solid or liquid system capable of generating gas or vapour is confined in an inert atmosphere, gas or vapour will be evolved into this atmosphere until its partial pressure reaches the equilibrium value appropriate to the prevailing temperature. Once equilibrium has been reached, measurement of the total gas pressure and analysis of the gas composition will clearly allow the equilibrium pressure over the solid or liquid system to be deduced. The inert gas may be made to flow over the solid or liquid, and if the process of vaporization is sufficiently rapid the emerging gas stream will contain the equilibrium partial pressure of the vaporized material, which may be collected from a known volume of the inert gas and weighed to determine the partial pressure. This 'entrainment' method lends itself particularly to the measurement of vapour pressure, dissociation pressures, etc., in systems in which the pressure cannot be directly applied to a suitable measuring device (as is often the case with measurements at high temperatures). It is also particularly applicable when the pressures to be measured are fairly low, because the use of an adequate volume of inert gas will always allow a weighable quantity of entrained material to be collected. A general discussion of the entrainment technique, with particular reference to high-temperature vapour-pressure measurements, has been given by Weibke and Kubaschewski[17]; typical applications are described by Jellinek *et al.*[18–20]

Successful use of the entrainment technique requires a high rate of vaporization from the solid or liquid system, so that the equilibrium partial pressure is maintained (or at least very closely approached) in the entraining inert gas. If the inert-gas flow rate is increased, a point is eventually reached at which the vaporization process cannot keep pace with the removal of vapour by entrainment; the partial pressure of the entrained vapour then drops below the equilibrium value. This effect of flow rate may often be allowed for by plotting the observed partial pressure against flow rate and extrapolating to zero flow rate; this procedure may not be accurate, however, because there is no clearly established relation between flow rate and pressure to determine the method of extrapolation. If an unduly low flow rate is used in entrainment experiments, the quantity of vaporized material transferred to the collection device by ordinary gas diffusion may be comparable with that entrained in the flowing gas stream, in which case an accurate correction for diffusion becomes difficult to derive.

In the reaction $SiO_2 + Si \rightleftharpoons 2SiO$, gaseous silicon monoxide is produced by reaction between solid silica and solid (or, at higher temperatures, liquid) silicon, and this reaction is necessarily very slow in comparison with the direct vaporization of a single substance. Thus, although the equilibrium pressure of silicon monoxide over a silica–silicon mixture can in principle be determined by entrainment, the effect of inert-gas flow-rate is expected to be large, and considerable extrapolation may be necessary. It will be shown that accurate application of the entrainment method to the silica–silicon system would require gas flow rates so low that the diffusion correction would become very large, and the rate of transfer of entrained silicon monoxide would be so small that its measurement would be very difficult. Experience of entrainment measurements indicates that extrapolated pressure values should correspond reasonably closely with the true values, but that undue significance should not be attached to the variation of extrapolated pressure with temperature.

### Furnace Equipment

The present research required production and measurement of temperatures in the range 1200°–1650° C. A standard Pt/Rh-wound electric tube furnace, with a tube 12 in. long by $1\frac{1}{4}$ in. internal dia., was used for temperatures up to 1350° C. A similar furnace with a larger tube (length 20 in., internal dia. 2 in.) was occasionally used for temperatures up to 1500° C. Both furnaces were supplied through standard power supply units, containing Sunvic thermal energy regulators.

Molybdenum-wound furnaces, with their heater windings protected by dry hydrogen, were used for temperatures in the range 1350°–1650° C. To reduce the consumption of hydrogen (or ' cracked ' ammonia) used to protect the molybdenum winding, special attention was given to the gaskets between the working tube (of sintered alumina) and the furnace casing, and between the main welded steel casing and the removable steel cover. The gasket used in the latter case was cut, to a suitable template, from $\frac{3}{16}$-in. thick sheet silicone rubber. The working-tube gaskets impose severe conditions of service, because the tube is held continuously at high temperatures for long periods; their temperature was reduced as far as possible by placing the gasketted joints close to the ends of the tube and by attaching a small water-cooling collar adjacent to each gasket (*see* Fig. 1). The gaskets were heavy silicone-rubber circular rings stretched over the tube and rolled down into position; when the tube was in place in the furnace these rings were squeezed into close contact with both tube and flange by screwing down the bolts on the flanges. These seals proved serviceable over long periods, and were sufficiently gas-tight to effect considerable economy in hydrogen consumption; a hydrogen flow-rate of 5 l./hr. was usually sufficient to maintain a slight positive pressure in the furnace casing. Excess hydrogen from the outlet was burned at a small jet.

### Temperature Measurements

Temperatures over the range 1200°–1500° C. (approx.) were measured by means of a standard Pt/Pt–Rh thermocouple, connected by suitable compensating leads to a Negretti and Zambra or Cambridge indicator with automatic cold-junction compensation. Higher temperatures were measured by a disappearing-filament pyrometer which, up to 1550° C., was calibrated against the thermocouple, the linear calibration plot being extrapolated to higher temperatures; a check of this extrapolation at the melting-point of pure quartz (1710° C.) proved it to be satisfactory.

Temperature measurements with the thermocouple were made with the junction against the outside surface of the working tube. The optical pyrometer was sighted, through a plane glass window suitably fitted at the end of the working tube, on the end of the sintered alumina boat containing the reacting mixture.

### Materials

Argon, used throughout as the entraining inert gas, was obtained in 100-cu. ft. cylinders; it was purified from water vapour and carbon dioxide by passing

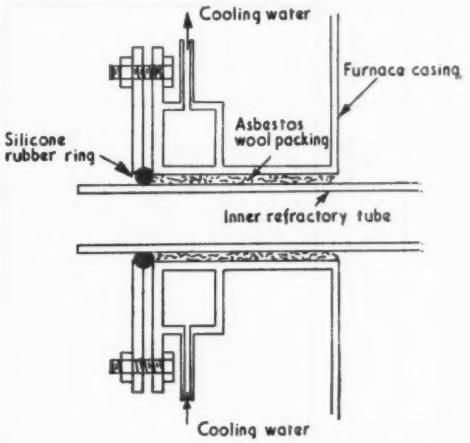


**Fig. 1—Gasket for end of molybdenum-wound furnace casing**

through $H_2SO_4$ bubblers, tubes of anhydrous magnesium perchlorate (Anhydrone), and tubes containing pellets of potassium hydroxide, and from traces of nitrogen by passing through a mixture of ignited calcium oxide (5 parts by weight) and magnesium powder (3 parts), held at 600° C. in a small electric furnace. Purification from nitrogen was necessary owing to the possible formation of silicon nitride from the silicon; the method used is due to Rayleigh,[21] and has proved entirely satisfactory. The heavy Pyrex glass tube containing the lime–magnesium mixture had to be kept at 600° C. continuously, as it invariably cracked on cooling. The purified argon was finally dried in another U-tube of Anhydrone, before use.

The silicon was a commercial ' fused lump ' grade, crushed to — 400 mesh in a rod mill and repeatedly extracted with hot concentrated HCl to remove iron. When the extract was free from iron the silicon was washed with distilled water, filtered off, and dried at 200° C. in an electric oven. The probable presence of some silica in the silicon was not harmful, and the usual hydrofluoric-acid extraction was omitted.

The silica used was an amorphous product (Neosyl), which was ignited at 1000° C. for 24 hr. before use. Crushed quartz was used for the later hydrogen reduction measurements, but it reacted too slowly for effective use in the silica–silicon reaction.

### Technique of Entrainment Measurements

The working tube in the furnace was of mullite (Triangle *H5*) or of sintered alumina; the latter, although less easily procured, proved much more satisfactory than mullite at higher temperatures. The ends of the working tube were closed by tightly fitting rubber bungs carrying gas inlet and outlet tubes; the bungs were shielded from the hot zone of the furnace by cylindrical radiation shields fashioned from refractory brick and pushed into the cool ends of the working tube. The purified and dried argon was passed in through a flowmeter of conventional design, employing dibutyl phthalate as manometric liquid. The flowmeter was calibrated for argon flow rates of up to 1·5 l./hr. by means of a standard gas-

Table I

ARGON ENTRAINMENT MEASUREMENTS ON THE REACTION $Si + SiO_2 \rightleftharpoons 2SiO$

Weight-Loss Method

| Run No. | Temperature, °C. (°K.) | Argon Flow Rate,* litres/hr. | Duration of Run, hr. | Observed Weight Loss, mg. | Diffusion Correction (No Flow), mg./hr. | Corrected Diffusion Correction For Run, mg. | Corrected Weight Loss, mg. | Entrained SiO, mg./litre | Entrained SiO, mg./litre, Extrapolated to Zero Flow Rate | $p_{SiO}$' atm. | $p_{SiO}$' mm. | $K_p$ ($p'_{SiO}$) | $\Delta G°$, kg.cal. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1300 (1573) | 0·62 | 7 | 19·0 | 0·75 | 3·6 | 15·4 | 3·55 | 5·0 | 0·0027 | 2·1 | $7·20 \times 10^{-4}$ | 37·0 |
| 2 | | 0·90 | 4·5 | 12·4 | | 1·6 | 10·8 | 2·67 | | | | | |
| 3 | | 1·30 | 5 | 12·0 | | 1·1 | 10·9 | 1·68 | | | | | |
| 4 | | 1·35 | 3·75 | 9·6 | | 0·8 | 8·8 | 1·74 | | | | | |
| 5 | 1350 (1623) | 0·65 | 8 | 67·1 | 4·9 | 29·6 | 37·5 | 7·2 | 8·7 | 0·0047 | 3·6 | $2·18 \times 10^{-3}$ | 34·6 |
| 6 | | 0·78 | 7 | 62·4 | | 25·2 | 37·2 | 6·6 | | | | | |
| 7 | | 0·95 | 7 | 63·1 | | 21·0 | 42·1 | 6·3 | | | | | |
| 8 | | 1·27 | 4 | 37·9 | | 10·0 | 27·9 | 5·5 | | | | | |
| 9 | 1380 (1653) | 0·61 | 9 | 73·6 | 4·3 | 26·1 | 47·5 | 8·7 | 12·2 | 0·0065 | 4·9 | $4·30 \times 10^{-3}$ | 33·1 |
| 10 | | 0·62 | 7 | 56·1 | | 18·9 | 37·2 | 8·6 | | | | | |
| 11 | | 0·90 | 4·5 | 37·0 | | 8·8 | 28·2 | 7·0 | | | | | |
| 12 | | 0·94 | 8 | 45·7 | | 15·2 | 30·5 | 6·7 | | | | | |
| 13 | | 1·08 | 4 | 31·9 | | 6·2 | 25·7 | 6·0 | | | | | |
| 14 | 1440 (1713) | 0·63 | 2 | 45·2 | 16·6 | 21·2 | 24·0 | 19·1 | 22·2 | 0·0119 | 9·1 | $1·42 \times 10^{-2}$ | 30·2 |
| 15 | | 0·63 | 2 | 47·9 | | 26·2 | 21·7 | 17·2 | | | | | |
| 16 | | 1·00 | 2 | 48·2 | | 16·6 | 31·6 | 15·8 | | | | | |
| 17 | | 1·09 | 2 | 51·5 | | 18·6 | 32·9 | 15·1 | | | | | |

* At 15° C. and 1 atm. pressure

meter. Argon leaving the working tube was allowed to escape through bubblers containing concentrated $H_2SO_4$, to prevent back-diffusion of air.

Two methods of measuring entrainment of silicon monoxide were employed. In the first, the loss in weight of the silica–silicon mixture due to loss of entrained silicon monoxide was determined directly by weighing the containing boat before and after passage of a known volume of argon (' weight-loss method '). In the second method, the entrainment gases were removed from the hot zone through a narrow aperture and were cooled, and the condensation products of the silicon monoxide were weighed (' collection method '). In the weight-loss method, corrections were necessary for silicon monoxide lost by diffusion; but in the collection method the entrained material could be collected separately from deposits formed by diffusion, and diffusion corrections were unnecessary.

In both methods, mixtures of composition $SiO_2 + Si$ were prepared by weighing out the constituents and mixing them thoroughly in an agate mortar. Several grams of the mixture were packed in a small sintered alumina boat (about 7 cm. × 1·5 cm. × 1 cm. internal dimensions) and placed in the furnace tube, which was evacuated by means of an oil-sealed rotary pump during the first stages of heating, to remove as much moisture as possible. When the furnace temperature reached about 300° C., argon was admitted, and a slow stream passed while the temperature was raised to 1200° C. or above. Heating was continued for several hours in the argon stream, to dry out the refractories and the reaction mixture as thoroughly as possible. Some silicon monoxide was, of course, produced during this preliminary heating, and condensed as a brownish mass in the cooler parts of the tube. The furnace was then cooled almost to room temperature with the slow argon stream still passing, and a run was begun by one of the methods described below.

The quantity of silicon monoxide volatilized during a run was very small in comparison with that of the silica–silicon mixture used, and several runs were usually carried out with the same batch of mixture; this eliminated the need for the preliminary drying before every run.

The total pressure in the reaction tube was 1 atm. throughout each run, and the temperature of gas measurement was 15° C. Small day-to-day variations from these values were neglected, in view of the rather low accuracy of the results.

*Weight-Loss Method*—The dried boat and contents were transferred to a desiccator and, when quite cool, were weighed as quickly as possible. The boat and mixture were replaced in the furnace tube, and the tube was evacuated during heating to about 300° C. Argon was then admitted to the tube until atmospheric pressure was reached. The furnace temperature was then raised as quickly as possible to the working value, and the argon stream started at the desired flow rate. The furnace temperature was hand-controlled during a run, and did not vary by more than ± 5°. The flow rate was also controlled by hand, a good reduction valve on the cylinder and a small auxiliary needle valve in the argon supply line

allowing the rate to be kept constant within about 1%. After the period required for the run, the furnace was turned off, the argon flow rate was reduced to a low value (some supply of gas being maintained to prevent air from being sucked into the tube on cooling), and after a suitable interval the boat was removed, cooled completely, and weighed.

*Collection Method*—The entrainment gases were led out of the furnace tube through a narrow sintered alumina tube (about 4 mm. internal dia.), which projected into the heated zone and terminated about 2 cm. from the end of the boat containing the silica and silicon. This alumina tube was connected to the glass exit tube, passing through the rubber bung at the end of the furnace tube, by means of rubber tubing, so that it could easily be detached and weighed. The hot end of the alumina tube was almost, but not quite, closed by pushing in a 5-cm. length of alumina rod of suitable diameter. The very narrow annular space between the rod and the tube provided a convenient aperture of small cross-section, which effectively prevented diffusion of silicon monoxide along the tube while allowing free passage of the flowing entrainment gases. These passed along the tube into a cool region, where the silicon monoxide condensed completely; by weighing the alumina tube before and after a run, the entrained and condensed silicon monoxide could be determined, no diffusion correction being necessary. A little diffused silicon monoxide condensed on the *outside* of the alumina tube, but was removed by gentle rubbing before the tube was weighed.

The procedure adopted in a run was similar to that already described, except that weighings of the boat were unnecessary. During the heating of the furnace to the desired working temperature, the argon stream was passed *into* the furnace system through the alumina tube; the gas stream was reversed (by the use of two-way taps) at the beginning of the run.

This method was of particular value in runs at the higher temperatures, in which melting and solidification of silicon in the boat caused some loss of material by spattering, with consequent losses in weight not due to entrainment or diffusion.

## RESULTS; DIFFUSION CORRECTION AND EXTRAPOLATION METHODS

The results obtained by the weight-loss and collection methods are shown in Tables I and II, respectively, which are largely self-explanatory.

Diffusion corrections in the weight-loss method were estimated by carrying out, at each of the temperatures at which entrainment measurements were made, several 'blank' experiments in which the furnace tube was filled with argon at approximately atmospheric pressure, but in which no flow of gas was maintained. The observed weight losses per hour, which were very consistent for successive 'blank' runs at the same temperature, represented loss of silicon monoxide by diffusion alone (*see* Table I). As expected, diffusion losses increased with temperature; the apparently anomalous drop shown in Table I between 1350° and 1380° C. results from a change to a larger furnace, in which the diffusion path between the boat and the nearest condensing surface was considerably longer.

The expected strong dependence of silicon monoxide entrainment on inert-gas flow rate is fully confirmed by the results in Tables I and II, and made necessary a careful consideration of extrapolation procedure. In the weight-loss method the corrections for diffusion were made in the following manner:

(i) The preliminary value of the weight loss corrected for diffusion was obtained by subtracting the diffusion correction $c_1$ for no flow, multiplied by $t$, the duration of the run, from the observed weight loss $w$. The effect of inert-gas flow is to reduce the operative partial pressure of silicon monoxide in the system, and hence to reduce the loss by diffusion; $w - tc_1$, based on the diffusion for no flow, is therefore an *over-corrected*

### Table II

**ARGON ENTRAINMENT MEASUREMENTS ON THE REACTION $Si + SiO_2 \rightleftharpoons 2SiO$**

**Collection Method**

(The duration of each run in this series was 1 hr.)

| Run No. | Temperature, ° C. (° K.) | Argon Flow Rate,* litres/hr. | Weight of Condensed SiO, mg. | Entrained SiO, mg./litre | Entrained SiO, mg./litre, Extrapolated to Zero Flow Rate | $P_{SiO}$, atm. | $P_{SiO}$, mm. | $K_p$ $(p^2_{SiO})$ | $\Delta G°$, kg.cal. |
|---|---|---|---|---|---|---|---|---|---|
| 18 | 1500 (1773) | 0·57 | 17·1 | 30·0 | 42·0 | 0·0221 | 16·8 | $4·87 \times 10^{-4}$ | 26·9 |
| 19 | | 0·59 | 18·6 | 31·5 | | | | | |
| 20 | | 0·75 | 19·2 | 25·5 | | | | | |
| 21 | | 0·91 | 23·0 | 25·5 | | | | | |
| 22 | | 0·98 | 21·7 | 22·0 | | | | | |
| 23 | 1580 (1853) | 0·54 | 45·5 | 84·0 | 93·5 | 0·0478 | 36·4 | $2·29 \times 10^{-3}$ | 22·4 |
| 24 | | 0·67 | 54·3 | 81·0 | | | | | |
| 25 | | 0·94 | 72·2 | 77·0 | | | | | |
| 26 | | 1·12 | 81·1 | 72·5 | | | | | |
| 27 | 1647 (1920) | 0·58 | 73·1 | 126·0 | 150·5 | 0·0747 | 56·7 | $5·59 \times 10^{-3}$ | 19·8 |
| 28 | | 0·81 | 92·7 | 114·5 | | | | | |
| 29 | | 0·88 | 96·8 | 110·0 | | | | | |
| 30 | | 1·04 | 109·8 | 105·5 | | | | | |

* At 15° C. and 1 atm. pressure

value of the weight loss. A preliminary value of the silicon monoxide entrainment $e_1$ was derived by dividing $w - tc_1$ by $ft$, the total volume of argon passed during the run.

(ii) The various values of $e_1$ obtained at one temperature were plotted against $f$, the argon flow rate. Each plot was approximately linear, and justified extrapolation of the best representative straight line to zero flow rate, giving a preliminary value $e_2$ for the 'entrainment' with no argon flow.

(iii) For each run, $c_1$ was multiplied by $e_1/e_2$, to give a new diffusion correction $c_2$ incorporating the effects of argon flow on the diffusion (but not the entrainment) process. This step involves the assumption that the loss of silicon monoxide by diffusion is proportional to its partial pressure.

(iv) The fully corrected weight loss $(w - tc_2)$ was derived for each run and divided by $ft$ to give the final value $e_3$ of silicon monoxide entrainment. The various values of $e_3$ should be fully corrected for the effects of diffusion, but they still show the effect of flow rate on the entrainment process.

In the collection method, the silicon monoxide entrainment was calculated for each run by dividing the weight of condensate by the total volume of argon passed, no diffusion corrections being necessary. The 'entrainment' extrapolated to zero flow of argon was determined at each temperature by plotting the values of silicon monoxide entrainment against argon flow rate. The plot was approximately linear at each temperature, and linear extrapolation, although involving a considerable flow-rate interval, was considered satisfactory.

The partial pressure of silicon monoxide at the working temperature was found by calculating, from the extrapolated entrainment value, the theoretical volume $v$, at 15° C. and 1 atm. pressure, of the gaseous silicon monoxide entrained by one litre of argon under similar conditions. For a total pressure of 1 atm. in the entrainment system, the silicon monoxide pressure $p_{SiO}$ is then equal to $v/(1 + v)$ atm. It is important to observe that the calculation of $v$ from a weight of silicon monoxide requires a value for the molecular weight of the gas, assumed to be 44 (*see* p. 77).

## THE EQUILIBRIUM $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$

The reduction of a heated metal oxide to the metal by means of hydrogen is a familiar type of reaction for which equilibrium data are readily obtained. For example, if $M$ represents a bivalent metal, the reaction may be written $MO + H_2 \rightleftharpoons M + H_2O$. If the metal and its oxide participate in the equilibrium as pure solids, their activities at a fixed temperature are taken to be unity, and the equilibrium constant (expressed in terms of gas pressures) is:

$$K_p = p_{H_2O}/p_{H_2}.$$

Provided that the metal and oxide are held at the fixed working temperature, 'back reaction' cannot occur, and the equilibrium mixture of hydrogen and water vapour may be led away into cool parts of the apparatus for analysis to determine $p_{H_2}$ and $p_{H_2O}$. The equilibrium $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$ is of a different type from that formulated above, because, under the temperature conditions contemplated, both products are gaseous and normal cooling of these products leads to reversal of the reaction and deposition of silica in the cooler parts of the apparatus; analysis of the equilibrium gas composition then becomes difficult. If silica is assumed to be present as the pure solid, the equilibrium constant is:

$$K_p = p_{H_2O} \cdot p_{SiO}/p_{H_2}.$$

However, if the starting materials are pure and dry, $p_{H_2O}$ and $p_{SiO}$ are necessarily identical, and the equilibrium constant may be written:

$$K_p = p^2_{H_2O}/p_{H_2}.$$

A survey of free-energy data indicated that the equilibrium partial pressures of water vapour and silicon monoxide from the reaction just formulated would be of the order of a few millimetres only. The product gases would therefore be extensively diluted with hydrogen, and the rate of recombination correspondingly diminished, which suggested that very rapid cooling of the products might inhibit reversal of the reaction. This was confirmed experimentally, rapid cooling of the hot gases from the silica–hydrogen reaction giving the usual brownish silicon monoxide condensate and a cold gas containing a measurable pressure of water vapour. Quantitative study of the equilibrium therefore appeared possible, but it was evident that it would require a rapid and reasonably accurate method of analysis for hydrogen mixed with a small partial pressure of water vapour. Thermal-conductivity analysers ('katharometers') were eventually used for this purpose.

The production of silicon monoxide by reduction of silica at a high temperature and its reoxidation at lower temperatures provides a potential mechanism of transfer of silica in any flow system in which sufficiently high temperatures exist. Such transfer was often observed during the present work; for example, passage of dry hydrogen through a heated sillimanite refractory tube produced a fluffy white deposit, proved by chemical analysis to be silica, at the point where the tube emerged from the heated zone of the furnace.

## ANALYSIS OF HYDROGEN/WATER-VAPOUR MIXTURES BY THERMAL-CONDUCTIVITY ANALYSERS

Thermal-conductivity methods of gas analysis are familiar[22] and do not require detailed description. Each specially designed analyser unit comprised four cells, each containing an electrically heated glass-coated filament, the temperature and resistance of which depended on the thermal conductivity of the gas filling the cell. Two cells were suitably incorporated in a flow system containing the gas to be analysed, and the other two were supplied with a current of hydrogen carefully dried by passage through tubes of anhydrous magnesium perchlorate (Anhydrone). The filaments in the four cells were interconnected in a Wheatstone bridge circuit in such a way that differences in thermal conductivity between the two gas streams unbalanced the bridge. The use of four cells, rather than two cells and fixed 'ratio arms,' allowed the unbalancing effect to be applied in both sides of the bridge circuit, so that the output current due to off-balance in the bridge circuit was larger. This current was measured by a standard Cambridge Type *B* recorder, giving a deflection proportional to the water-vapour content of the 'wet'

hydrogen. The recorder chart had a time scale of ½ in./hr., which was convenient for runs of the customary duration. Accurate recording of the gas composition, over the period of several hours normally needed for a series of measurements, required a constant current supply to the bridge circuit; this was obtained from accumulators, which were voltage-stabilized by trickle-charging at a current approximately equal to that taken by the analysers (about 0·35 amp.). By leaving charger and analysers permanently connected to the accumulators, steady conditions were maintained and the current supply remained constant. The actual bridge-circuit current was adjusted by means of a variable resistance and standardizing device built into the recorder. A provision for zero adjustment in the analyser bridge circuit allowed the bridge to be balanced accurately, before measurements were made, with dry hydrogen in all four cells. This zero adjustment varied slightly with the flow rate of gas through the cells, and was checked whenever the flow rate used during calibration or measurements was changed.

The analyser system required calibration with hydrogen and water-vapour mixtures of known composition. For this purpose, dry hydrogen was passed through a calibrated flowmeter and then bubbled through a long column of saturated calcium chloride solution (containing excess of the solid hexahydrate) in a glass cylinder immersed in a thermostat bath; the issuing gas, containing water vapour at the saturation pressure of the calcium chloride solution, was passed through the analyser, through two absorption tubes containing anhydrous magnesium perchlorate (Anhydrone) to absorb water vapour, and into a standard gas meter to measure the hydrogen. A suitable system of taps allowed the absorption tubes to be by-passed and removed without interruption of the gas stream. By adjustment of the thermostat temperature the water vapour pressure could be varied between the convenient limits of 4·5 and 7·5 mm. Five calibration points were obtained in this range. For each point, the thermostat temperature was suitably regulated and hydrogen was passed until the recorder showed a steady deflection; the absorption tubes were then weighed before and after a run of several hours' duration, during which measurements of hydrogen volume were made from the gas meter and (as a check) from the flowmeter. The partial water-vapour pressures, calculated from the weights of absorbed water and suitably corrected hydrogen volumes, were then plotted against corresponding recorder deflections for the successive calibration runs; an accurately linear plot, passing through the origin, was obtained.

Thermal conductivity analysers record the ratio of partial pressures of water vapour to hydrogen, irrespective of small variations in total gas pressure; for convenience, the calibration measurements were corrected to represent the pressure of water vapour admixed with hydrogen at 1 atm. partial pressure. The recorder was found to give a deflection of about 65 mm. for 10 mm. of water vapour, which allowed assessment of water pressures, from the recorder chart, to better than $\pm$ 0·1 mm.

Frequent use of thermal conductivity analysers in several research applications has proved their usefulness in the analysis of simple binary gas mixtures, particularly in flow systems. In the case of hydrogen and water vapour, the alternative method of analysis, involving absorption and weighing of water from a measured volume of gas, usually involves runs of long duration to accumulate sufficient water for accurate weighing; moreover, the weighing gives only an average water content for the whole period of collection. Thermal-conductivity analysers give an immediate and accurate indication of the water content, and reproduce its variation over a period of time. However, the high thermal conductivity of hydrogen makes the method particularly sensitive with mixtures containing hydrogen, and corresponding sensitivity may not readily be attainable with other gases.

**Equilibrium Measurements**

The furnace and temperature-measuring equipment were those used for investigating the silicon–silica reaction (*see* p. 71), but the reducibility of mullite and other siliceous refractories in dry hydrogen made it essential to use a sintered alumina working tube for all measurements on the silica–hydrogen system. The silica was selected from large crystals of high-quality quartz, the selected pieces being crushed to pass a 100-mesh sieve. Finer grinding of the quartz proved inadvisable, because it facilitated sintering and consequent loss of reactivity, particularly at the higher temperatures.

The powdered quartz was spread in a shallow layer on the bottom of a sintered alumina boat, with which no appreciable slagging was observed except at the highest temperatures; the boat was placed in the middle of the heated zone of the working tube, and the optical pyrometer focused on its end. Hydrogen was purified and dried by passing it successively through palladinized asbestos at 350° C., concentrated sulphuric acid, potassium hydroxide pellets (to remove traces of sulphurous gases from the acid), and Anhydrone. The dry hydrogen was passed through the 'dry' side of the analyser and into the working tube. After passing over the silica, the gas stream was led out through a narrow sintered alumina tube (5-mm. bore), projecting well into the heated zone and containing a loosely fitting alumina rod. The gas mixture (hydrogen, water vapour, and silicon monoxide) thus emerged from the equilibrium region through a tube of very small 'dead space'; this produced a high streaming velocity from the hot to the cold parts of the apparatus, and promoted the rapid cooling necessary to prevent appreciable reversal of the reaction.

Before measurements were begun, the working tube and connecting tubing were evacuated during slow heating of the furnace to 1200° C. (using a suitable arrangement of taps in the flow system). Dry hydrogen was then admitted and allowed to flow through the system at a predetermined flow rate of 1–2 l./hr. The analyser recorder was started when hydrogen flow had become steady, and after 30–40 min. at a steady temperature it normally showed a constant water content in the exit gases from the

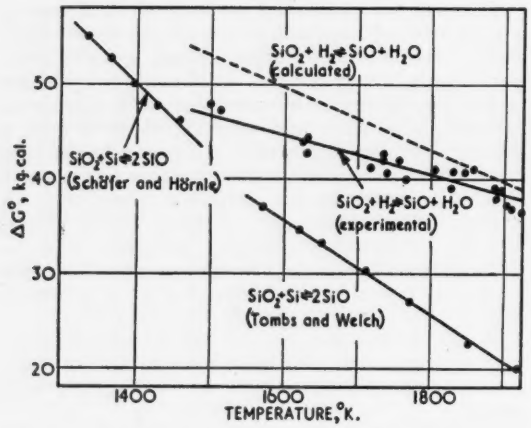


**Fig. 2—Standard free-energy curves for reactions involving silicon monoxide**

furnace system. Steady conditions were maintained for 10–15 min., to ensure that true equilibrium had been reached. Similar readings were taken at 50° intervals up to about 1650° C. The chart from the recorder showed a series of steps representing the equilibrium water-vapour contents corresponding to the successive constant temperatures, and the chart readings were converted, using the calibration curve, into partial water-vapour pressures referred to a hydrogen partial pressure of 1 atm.

The temperature limits, 1200° and 1650° C., of the measurements were set by the very low water-vapour pressures recorded at lower temperatures, and by the marked tendency for the silica to sinter, or to form a slag with the refractory boat, at higher temperatures.

Inhibition of the back-reaction between silicon monoxide and water vapour was confirmed by testing the effect of hydrogen flow rate on the measured partial pressure of water vapour. Changes in the flow rate in the range 1–2·5 l./hr., for a constant reaction temperature, produced no measurable change in the water-vapour content of the exit gases. No deposition of silica by a back-reaction was ever detected, but the expected deposit of brownish silicon monoxide condensate appeared in the exit tube.

The results of the measurements are given in Table III. The values of $K_p$ in column 6 are equal to $p^2_{H_2O}/p_{H_2}$ (*see* p. 74), $p_{H_2O}$ being expressed in atmospheres and $p_{H_2}$ being 1 atm. in all cases.

## GENERAL DISCUSSION OF RESULTS

Values of standard free-energy changes derived from the relation $\Delta G^\circ = -RT\log_e K_p$ are given in the final columns of Tables I, II, and III, and are shown graphically in Fig. 2 as a plot of $\Delta G^\circ$ against $T$.

### Data for the Reaction $SiO_2 + Si \rightleftharpoons 2SiO$

The standard free-energy changes for this reaction fall satisfactorily on a linear $\Delta G^\circ/T$ plot, as indicated in Fig. 2. The line can be represented by the expression $\Delta G^\circ = 117{\cdot}1 - 0{\cdot}0509\ T$ kg.cal.; it should show a small reduction of gradient at the melting point of silicon (1688° K.), but this change cannot be plotted from the available points. The entropy change on fusion of silicon is not known with sufficient certainty for the change of slope to be inserted by calculation.

The satisfactory agreement between results from the two methods of entrainment measurement is evident from Fig. 2, but it is very difficult to assess the absolute accuracy of the equilibrium pressures

## Table III

**PARTIAL PRESSURES OF WATER VAPOUR IN EQUILIBRIUM GAS FROM THE REACTION $SiO + H_2 \rightleftharpoons SiO + H_2O$**

| Run No. | Temperature | | $p_{H_2O}$, mm. | $p_{H_2O} \times 10^3$, atm. | $K_p \times 10^4$ | $\Delta G^\circ$, kg.cal. |
|---|---|---|---|---|---|---|
| | °C. | °K. | | | | |
| 1 | 1228 | 1501 | 0·25 | 0·33 | 0·108 | 47·8 |
| 2 | 1241 | 1514 | 0·30 | 0·40 | 0·156 | 47·1 |
| 3 | 1355 | 1628 | 0·86 | 1·13 | 1·28 | 43·9 |
| 4 | 1360 | 1633 | 0·83 | 1·09 | 1·19 | 44·3 |
| 5 | 1360 | 1633 | 0·86 | 1·13 | 1·28 | 44·0 |
| 6 | 1360 | 1633 | 1·05 | 1·38 | 1·91 | 42·7 |
| 7 | 1446 | 1719 | 1·85 | 2·43 | 5·93 | 41·1 |
| 8 | 1464 | 1737 | 1·60 | 2·11 | 4·43 | 42·5 |
| 9 | 1464 | 1737 | 1·75 | 2·30 | 5·30 | 41·9 |
| 10 | 1469 | 1742 | 2·14 | 2·82 | 7·93 | 40·6 |
| 11 | 1485 | 1758 | 1·88 | 2·47 | 6·12 | 41·9 |
| 12 | 1495 | 1768 | 2·58 | 3·39 | 11·5 | 39·9 |
| 13 | 1539 | 1812 | 2·58 | 3·39 | 11·5 | 40·9 |
| 14 | 1556 | 1829 | 3·59 | 4·72 | 22·3 | 38·9 |
| 15 | 1559 | 1832 | 2·78 | 3·66 | 13·4 | 40·8 |
| 16 | 1575 | 1848 | 3·01 | 3·96 | 15·7 | 40·6 |
| 17 | 1587 | 1860 | 3·00 | 3·95 | 15·6 | 40·9 |
| 18 | 1618 | 1891 | 4·28 | 5·63 | 31·7 | 38·9 |
| 19 | 1618 | 1891 | 5·00 | 6·58 | 43·3 | 37·8 |
| 20 | 1625 | 1898 | 4·44 | 5·84 | 34·1 | 38·8 |
| 21 | 1633 | 1906 | 5·75 | 7·57 | 57·3 | 37·0 |
| 22 | 1639 | 1912 | 6·04 | 7·95 | 63·2 | 36·7 |
| 23 | 1653 | 1926 | 6·57 | 8·65 | 74·7 | 36·4 |

determined by entrainment. High accuracy cannot reasonably be claimed, because of the long extrapolation to zero flow rate. Study of the extrapolated plots suggests that values of $p_{SiO}$ should be accurate to $\pm 20\%$, corresponding to a probable error of approximately $\pm$ 1·5 kg.cal. in the recorded values of $\Delta G^\circ$.

For purposes of comparison, $\Delta G^\circ$ values derived from the effusion measurements of Schäfer and Hörnle[6] on the same system, but over a lower temperature range, are shown in Table IV and plotted in Fig. 2. The earlier results of Gel'd and Kochnev[12–14] differ widely from those of Schäfer and Hörnle and from the present results, the discrepancy being less at the higher temperatures. Schafer and Hornle consider that a proper effusion equilibrium was not established in the experiments described by Gel'd and Kochnev, and this view is supported by the very low rate of volatilization of silicon monoxide from silicon–silica mixtures in the entrainment measurements described in this paper. As expected, pressure values derived from the data of Gel'd and Kochnev are consistently much lower than those given in Tables I, II, and IV. In view of the large temperature range covered by Fig. 2, and the necessarily rather low accuracy of the measurements, the agreement between the results of Schäfer and Hörnle and those now reported is satisfactory, the most significant discrepancy being a difference in the slope of the linear $\Delta G^\circ/T$ plots. The expected changes of specific heat with temperature would make the $\Delta G^\circ/T$ curves slightly convex downwards; introduction of specific heat data, therefore, should improve still further the agreement between the two sets of results.

Perhaps the most important conclusion to be drawn from the general agreement between effusion and entrainment measurements is that gaseous silicon monoxide exists predominantly as simple SiO molecules. The expressions used to calculate $p_{SiO}$ in the two methods contain the molecular weight of the gas in different forms, and the assumption of an incorrect value would at once introduce a major discrepancy between the two sets of pressure values. The possibility of appreciable polymerization of SiO molecules in the gas is therefore discounted.

The slopes of the linear $\Delta G^\circ/T$ plots in Fig. 2 may be regarded as representing approximately the entropy changes accompanying the reactions to which the $\Delta G^\circ$ data refer (*see* Richardson and Jeffes,[23] p. 262). The value given by the entrainment data (for $SiO_2 + Si \rightleftharpoons 2SiO$) is + 50·9 g.cal./° C. In Fig. 2 the straight line drawn through Schäfer and Hörnle's measurements corresponds to the expression $\Delta G^\circ = 156{\cdot}9 - 0{\cdot}0763T$, giving an entropy change of + 76·3 g.cal./° C. The standard entropy values at 298° K. for quartz, silicon, and gaseous silicon monoxide, respectively, are 10·0, 4·5, and 50·6 g.cal. per ° C. g.mol. (Kelley[24,25]); these give an entropy change of + 86·7 g.cal./° C. for this reaction. Schäfer and Hörnle's line is therefore in better agreement with established entropy data. Undue weight should not, however, be given to this comparison, because an entropy change assessed from the gradient of a $\Delta G^\circ/T$ line is a mean value for a temperature range within which the heat content and entropy changes for the reaction

**Table IV**

**MEASUREMENTS ON THE EQUILIBRIUM $Si + SiO_2 \rightleftharpoons 2SiO$ BY EFFUSION**

| Temp., ° K. | $p_{SiO}$, mm. | $p_{SiO}$, atm. | $K_p$ ($p^2_{SiO}$) | $\Delta G^\circ$, kg.cal. |
|---|---|---|---|---|
| 1336 | 0·0238 | $3{\cdot}13 \times 10^{-5}$ | $9{\cdot}81 \times 10^{-10}$ | 55·0 |
| 1367 | 0·0467 | $6{\cdot}14 \times 10^{-5}$ | $3{\cdot}78 \times 10^{-9}$ | 52·7 |
| 1398 | 0·0914 | $1{\cdot}20 \times 10^{-4}$ | $1{\cdot}45 \times 10^{-8}$ | 50·1 |
| 1429 | 0·1701 | $2{\cdot}24 \times 10^{-4}$ | $5{\cdot}01 \times 10^{-8}$ | 47·7 |
| 1460 | 0·2634 | $3{\cdot}47 \times 10^{-4}$ | $1{\cdot}20 \times 10^{-7}$ | 46·2 |

are assumed, by implication, to remain constant. This assumption is scarcely justified in a comparison of values referring to temperatures more than 1000° apart; expected changes of entropy with temperature would, in fact, reduce the discrepancies between the values just quoted. The absence of specific heat data for gaseous silicon monoxide makes a comparison of entropy data difficult over the actual temperature range of the measurements.

### Data for the Reaction $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$

The points on the $\Delta G^\circ/T$ plot for this reaction show considerable scatter, owing to traces of moisture introduced into the gas stream during the measurements. The values of $K_p$ shown in Table III are calculated by assuming that $p_{SiO}$ and $p_{H_2O}$ are equal, *i.e.*, that all water vapour appearing in the product gases is derived by reduction of silica. Inevitable desorption of water from refractories, glass tubing, etc., in the flow system probably introduces small and variable amounts into the gas stream. The recorded values of $K_p$ are therefore likely to be too high, and the corresponding points in Fig. 2 too near the temperature axis. Since measured values of $p_{H_2O}$ were as low as 0·25 mm. (at 1228° C.), the errors may be substantial at the lower temperatures of measurement; they should be considerably smaller at the higher temperatures, where $p_{H_2O}$ values of 5–6 mm. were recorded.

Combination of data for the reaction (*a*) $SiO_2 + Si \rightleftharpoons 2SiO$ with standard free-energy change expressions for the reactions (*b*) $2H_2 + O_2 \rightleftharpoons 2H_2O$ and (*c*) $Si + O_2 \rightleftharpoons SiO_2$ yields a $\Delta G^\circ/T$ relation for the reaction (*d*) $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$. The following expressions are used for this purpose:

$$\Delta G^\circ_a = 117{\cdot}1 - 0{\cdot}0509T \quad (\textit{see} \text{ p. 76})$$

$$\Delta G^\circ_b = -118{\cdot}0 + 0{\cdot}0268T \quad \text{(Richardson and Jeffes,[23] p. 267)}$$

$$\Delta G^\circ_c = -208{\cdot}3 + 0{\cdot}0433T \quad \text{(Richardson and Jeffes,[23] p. 269)}$$

These give:

$$\Delta G^\circ_d = 103{\cdot}7 - 0{\cdot}0337T.$$

The straight line corresponding to this expression is shown dotted in Fig. 2. In view of the admittedly low accuracy of the experimental points at the lower temperatures, the agreement with experiment is satisfactory. The expression quoted for $\Delta G^\circ_c$ is of only moderate accuracy, and on this ground alone closer agreement could scarcely be expected. It is

concluded, therefore, that the entrainment data given on p. 76 and embodied in the expression for $\Delta G^\circ_a$ are in satisfactory agreement with the measurements on the silica–hydrogen equilibrium.

The present results differ somewhat from those of Grube and Speidel[11] on the same equilibrium. It seems likely that in their measurements appreciable quantities of silicon monoxide escaped determination, possibly by back-diffusion against the entraining hydrogen stream.

## GENERAL CONCLUSIONS

Although more accurate measurements may lead to small changes, particularly in the gradient of the $\Delta G^\circ/T$ line shown in Fig. 2, the $\Delta G^\circ$ values given for the reaction $SiO_2 + Si \rightleftharpoons 2SiO$ may be used with reasonable confidence in predicting the occurrence and behaviour of gaseous silicon monoxide at high temperatures. Addition of the expression given above for $\Delta G^\circ_c$ affords an expression for the standard free energy of formation of gaseous silicon monoxide from silicon and oxygen:

$$2Si + O_2 \rightleftharpoons 2SiO; \quad \Delta G^\circ = -91{\cdot}2 - 0{\cdot}0076T.$$

On this basis, free-energy data for silicon monoxide may be compared with similar data for other oxides in a chart of the type advocated by Richardson and Jeffes[23]; the silicon monoxide line on such a chart then becomes one of the very few having a negative gradient. Although it lies well above the silica line at low temperatures, the gradients are such that the two lines cross just below 2000° C. Even at steelmaking temperatures, silica and silicon monoxide are of comparable stability, and the monoxide cannot be neglected as a participant in oxidation–reduction equilibria involving silica and silicon.

A further paper is in preparation on the occurrence of silicon monoxide in silicon equilibria in liquid iron, already considered in a preliminary manner by Zapffe and Sims.[4, 7] The results now reported establish that silicon monoxide may be expected as a normal product of reduction of silica (or silicates) at temperatures in and above the steelmaking range, and the thermodynamic data given are sufficient to predict the behaviour of silicon monoxide in at least the simpler reactions.

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# Determination of Combined Carbon in Graphitic Iron

*By the Methods of Analysis Committee*


## SYNOPSIS

An examination of methods of determining combined carbon in graphitic iron has been carried out; as a standard procedure, derivation of the combined carbon by difference following separate determinations of total and graphitic carbon is preferred to the direct procedures which have been investigated. The use of solid samples for both total and graphitic carbon is recommended; drillings tend to give low results for both these constituents owing to the loss of graphite as a fine dust.

The difficulties in sampling high-carbon, coarse-graphite iron are emphasized, and the use of a hollow mill to prepare solid specimens of suitable size and weight from various points in a casting is proposed.


During the course of a research on the composition of cast-iron ingot moulds, it was felt desirable that the method used for the determination of combined carbon should be approved or recommended by a representative analytical body. The Pig Iron, Carbon and Low Alloy Steels Analysis Sub-Committee was requested to make suitable recommendations for such a method and this report summarizes its work on this project with appropriate conclusions.

The constitution of the Sub-Committee at 30th September, 1951, was as follows:

| | |
|---|---|
| S. W. Craven (*Chairman*) | I.C.I., Ltd., Alkali Division |
| O. Beadle | Cargo Fleet Iron Co., Ltd. |
| L. E. Gardner | Edgar Allen and Co., Ltd. |
| C. L. Grayson | English Steel Corporation, Ltd. |
| R. F. Jones | Steel Co. of Wales, Ltd. |
| J. McCrosson | Lanarkshire Steel Co., Ltd. |
| A. W. Reed | Consett Iron Co., Ltd. |
| N. D. Ridsdale | Bureau of Analysed Samples, Ltd. |
| C. W. Short | John Lysaght, Ltd. |
| F. Speed | Dorman Long and Co., Ltd. |
| H. J. Turner | Steel, Peech and Tozer |
| W. Westwood | British Cast Iron Research Association |


The Sub-Committee also acknowledges the valuable assistance received from the following past members:

| | |
|---|---|
| J. H. Wright (*Chairman*, 1946–49) | Dorman Long and Co., Ltd. |
| W. F. Charteris | Colvilles, Ltd. |
| J. M. Harrison | Lancashire Steel Corporation, Ltd. |
| J. D. Hill | Bragg Laboratory, N.O.I.D. |


## REVIEW OF THE PROBLEM

The determination of carbon in large castings with coarse graphite structures, such as ingot moulds, is a very difficult problem and sampling is of paramount importance. Such castings are always prone to heterogeneity, so that it is practically impossible for a single sample to be representative of the casting as a whole. Therefore analytical figures should be related to the position from which the sample was taken and not accepted without reserve as the average composition of the casting.

A further difficulty is that with sampling by milling or drilling there is a danger that fine dust, rich in graphite, will be lost. Such losses may be minimized by drilling with a fine drill at a very slow speed (about 25 r.p.m.) or by using small, solid pieces of the material as samples.[1, 2]

Bulk samples almost always consist of a heterogeneous mixture of fine and coarse particles differing widely in carbon content. The analytical sample selected from the bulk sample must therefore contain the correct proportion of the various particle sizes. The following recommendations ensure that a representative sample is taken:

(i) Separate the bulk sample into two or more fractions by sieving, taking care that none of the fine particles are lost, then weigh all the fractions. For the analytical sample take the correct proportion of each fraction

(ii) Reduce the whole sample to as uniform a size as possible by crushing

(iii) Take a small sample, by means of a fine drill operating at a very slow speed, and use the whole of it for one determination

(iv) Use the whole of a selected solid test piece as an analytical sample.

As the loss of fine dust during crushing and sieving is almost unavoidable, (i) and (ii) are not entirely satisfactory.

In this investigation specially prepared samples of uniform particle size, from which the fine material had been removed, were used. In this way it was hoped to divorce chemical techniques from sampling errors and to establish the relative accuracy and reproducibility of the different procedures under the most favourable conditions.

## METHODS AVAILABLE

The most widely practised procedure for the determination of combined carbon is the indirect method involving separate determination of total carbon and graphitic carbon, the combined carbon being the


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difference between these two results. This method has several drawbacks, *viz.*:

(1) It is comparatively time-consuming
(2) The burden of any errors made in determining either total or graphitic carbon falls upon the result for combined carbon
(3) Any inconsistencies in composition between the two samples used for determining the total and graphitic carbon will be reflected in the combined-carbon figure.

In view of the need for rapid, accurate, and trustworthy determinations of combined carbon, attention was given to two direct methods already in existence.*

(1) The colorimetric (or Eggertz) method depends on the formation of a brown compound when the carbides react with nitric acid. Unfortunately, the colour produced is not directly proportional to the combined-carbon content; it varies considerably with the form in which the carbon exists in the sample, and is sensitive to light. The strength of the nitric acid used, the time to effect solution, the temperature at which it is carried out, and the composition and metallurgical history of the sample also influence the reaction. While the procedure can give comparative results for different batches of the same class of iron, it was too unreliable for materials of varying composition and no experimental work was carried out.

(2) Details have been published in America of a direct method worked out by J. G. Donaldson.[3] The reaction is carried out in a closed system, the sample being dissolved in a dilute solution of nitric–sulphuric–phosphoric acid, containing a small amount of silver nitrate as a catalyst. The carbonaceous gases initially evolved are passed over heated copper oxide and the carbon dioxide produced is absorbed. The carbon still remaining in solution is next oxidized with ammonium persulphate, the solution is boiled, and the evolved gases are treated as before. The absorbed carbon dioxide is then weighed and calculated as combined carbon. The author claimed that the method was rapid and accurate, giving results in better agreement, in precision and accuracy, than those obtained by indirect procedures, and with considerable saving in time. This technique seemed to merit detailed examination; the experimental work carried out on it and on the difference method are described in the following section. By comparison with the difference method, Donaldson's procedure requires rather complicated and expensive all-glass apparatus. One apparatus was lost as the result of an explosion during the initial solution of the sample, believed to be due to the formation of a small amount of pyrophoric iron with subsequent ignition of the hydrogen–oxygen mixture in the flask.

## EXPERIMENTAL WORK

### The Donaldson Direct Method

Since several members did not possess the apparatus for a complete examination of Donaldson's method, a study was first made of the action of the solvent mixture proposed on specially prepared samples whose graphite content had been carefully established.

Donaldson's solution procedure consists of dissolving the sample in 40 ml. of a mixture of 5·25 g. of silver nitrate, 1800 ml. of water, 500 ml. of nitric acid (sp.gr. 1·42), 160 ml. of sulphuric acid (sp.gr. 1·84), and 200 ml. of phosphoric acid (sp.gr. 1·75), completing the oxidation of the combined carbon by boiling after the addition of 5 g. of ammonium persulphate dissolved in 100 ml. of water. If the determination of combined carbon is to be accurate no attack at all on graphite must take place; any conversion of graphite to carbonaceous gas would lead to high results for combined carbon. By using Donaldson's solution method, filtering off and determining the residual graphite, in some cases graphite was definitely attacked. For example, repeated determinations of graphite on one standard sample of cast iron using nitric acid (sp.gr. 1·20) as solvent gave a set of figures closely grouped round 2·0%. Six analysts made graphite determinations on this sample after solution in Donaldson's mixture and obtained results of 1·78, 1·65, 1·93, 1·62, 1·72, and 1·68%. By omitting the addition of ammonium persulphate one analyst increased his recovery of graphite from 1·65 to 1·92%. Some attack on graphite when using the Donaldson method has been observed by other workers. Schwartz and Guiler[4] suggest that this might be due either to the friable character of temper carbon or to its chemical activity.

In the experimental work with the complete Donaldson apparatus difficulty was experienced in obtaining ' blanks ' which were low and reproducible. Numerous modifications gave some improvement, but whilst it was possible to obtain more accurate results with a revised technique, which was laborious and tedious, ' blank ' trouble still persisted. Furthermore, the direct method did not offer any advantages in speed, as had been claimed.

One of the major variations investigated was a change in solution technique prompted by the observation that the ammonium persulphate addition seemed to be chiefly responsible for the attack on graphite. The procedure adopted was:

(1) Treatment of the sample with Donaldson's diluted sulphuric–nitric–phosphoric acid mixture and absorption of the gases evolved
(2) Filtration to remove graphite, which was then determined separately by combustion in oxygen
(3) Return of the filtrate to the original apparatus followed by treatment with ammonium persulphate to complete the oxidation of residual carbon compounds.

This method offers the advantage that both combined and graphitic carbon can be determined on the same sample weight, but the Sub-Committee researches failed to establish it on a foundation sound enough to warrant its recommendation as a standard method.

### The Difference Method

*Determination of Total Carbon*—Methods for determination of total carbon include direct dry combustion, wet oxidation to carbon dioxide, or wet separation of all forms of carbon prior to combustion. The resulting carbon dioxide may be determined either by gravimetric absorption or by various volumetric and gas-analysis methods. Of these alternatives attention was focused on direct combustion of the whole sample in purified oxygen, followed by absorption and weighing of the purified carbon dioxide produced, which corresponds to the total carbon present in the sample.

* Methods depending upon changes of electrical and magnetic properties are not applicable to cast iron.

**Table I**

**DETERMINATION OF COMBINED CARBON (%) (DIFFERENCE METHOD)**

| Operator | Plain Cast Iron | | | Alloy Cast Iron* (0·37% Ti, 0·6% V) | | | Alloy Cast Iron* (1·3% Cr) | | |
|---|---|---|---|---|---|---|---|---|---|
| | T.C. | G.C. | C.C. | T.C. | G.C. | C.C. | T.C. | G.C. | C.C. |
| A | 2·80 | 1·99 | 0·81 | 3·85 | 1·97 | 1·88 | 2·41 | 1·14 | 1·27 |
| B | 2·74 | 1·91 | 0·83 | 3·78 | 1·90 | 1·88 | 2·48 | 1·13 | 1·35 |
| C | 2·77 | 1·95 | 0·82 | ... | ... | ... | ... | ... | ... |
| D | ... | ... | ... | ... | ... | ... | 2·39 | 1·09 | 1·30 |
| E | 2·79 | 1·99 | 0·80 | 3·78 | 1·96 | 1·82 | 2·37 | 1·04 | 1·33 |
| F | 2·81 | 1·94 | 0·87 | ... | ... | ... | ... | ... | ... |
| G | ... | ... | ... | 3·75 | 1·90 | 1·85 | 2·42 | 1·09 | 1·33 |
| H | 2·79 | 2·00 | 0·79 | ... | ... | ... | ... | ... | ... |
| I | ... | ... | ... | 3·70 | 1·92 | 1·78 | 2·37 | 1·03 | 1·34 |
| J | 2·80 | 1·99 | 0·81 | 3·79 | 1·99 | 1·80 | 2·39 | 1·13 | 1·26 |
| K | 2·78 | 1·96 | 0·82 | ... | ... | ... | ... | ... | ... |
| Average | 2·79 | 1·97 | 0·82 | 3·78 | 1·94 | 1·84 | 2·40 | 1·09 | 1·31 |

* Residues from these samples were examined for Ti, V, and Cr, but negative results were obtained

Several details of this direct gravimetric combustion method for total carbon were investigated, including combustion temperatures between 1000° and 1300° C., various fluxes and accelerators such as tin, red lead, and lead chromate, and various types of combustion trains and absorbents. The method finally employed closely followed B.S. 1121: Part 11: 1948, and the results obtained for total carbon in the different samples circulated to members are given in Table I.

*Determination of Graphitic Carbon*—For this determination the choice of methods is very limited. The accepted method is to dissolve the sample in dilute nitric acid, which leaves graphite unattacked. The graphite is subsequently separated on a carbon-free filter, washed, dried, and determined by direct combustion as described above. Accuracy of the method depends on complete solution of the various carbides and entire absence of attack on the graphite. In alloy cast irons some doubt existed as to whether certain carbides, such as those of Cr, were completely decomposed by the nitric acid solvent. Experimental work, however, has shown that:

(*a*) With irons containing up to 1·5% of Cr and 0·4% of Ti, complete decomposition is achieved; the graphite residue in the samples investigated (Table I) did not include carbides of either Cr or Ti

(*b*) No appreciable attack takes place on the dried and weighed residue after a further period of digestion in nitric acid, indicating that graphite is not affected by this solvent.

Consideration was given to the choice of a suitable filtering medium, alternatives proposed being:

(*a*) Ignited asbestos in a glass, silica, or porcelain filtering crucible (Gooch type), the asbestos and residue being subsequently transferred to an ignited boat for combustion

(*b*) As in (*a*), but using a crucible small enough to be inserted directly into the combustion tube

(*c*) A crucible with a sintered silica disc, followed as in (*b*) by direct combustion of the residue *in situ*

(*d*) Porous Alundum thimbles for direct ignition.

Initial experiments with silica-grid filtration crucibles indicated that, with the sizes usually available, filtration was an unduly tedious and delicate operation, and a recommendation was made that crucibles of greater capacity, still capable of being inserted in combustion tubes of standard size, should be manufactured for this purpose.

Appreciable variations in available supplies of asbestos wool or fibre gave rise to doubts of the suitability of (*a*) and (*b*) as part of a standard procedure, but after several trials it was felt that the use of asbestos as a filtering medium would be more satisfactory than a sintered silica disc of fine porosity. Choice of the latter was considered unwise after trials of various samples had shown that complete removal of the unattacked graphite was not always obtained in a reasonable operating time and that discs of fine porosity quickly became permanently blocked. This was considered to be due to variations both in the size of the graphite particles and in the porosity of the filter discs. The results obtained were as follows:

| | Nominal Porosity, μ | | | |
|---|---|---|---|---|
| | 90–150 | 40–90 | 15–40 | 5–15 |
| **Time for Filtration and Washing (100 ml. approx.)** | | | | |
| (*a*) | 15 min. | 1 hr. | ... | 2 hr. |
| (*b*) | ... | 2 hr. | 1 hr. | 1 hr. |
| (*c*) | 1 hr. | 30 min. | 30 min. | ... |
| (*d*) | Very rapid | ... | 30 min. | 2 hr. |
| **Insoluble in Filtrate** | | | | |
| (*a*) | Considerable | Trace | ... | Nil |
| (*b*) | ... | Appreciable | Trace | Nil |
| (*c*) | Nil | Nil | Nil | ... |
| (*d*) | Considerable | ... | Trace | Nil |

Approaches have been made to manufacturers and to the appropriate B.S.I. Technical Committee on the matter of closer standardization of filtration rate and porosity of these crucibles. A suitable specification has recently been published[5] and investigation of the properties of the standard discs will be required before new recommendations can be made.

The most suitable type of asbestos examined was a sample free from long, coarse fibres, which did not disintegrate or contain excessive ' fines ' after ignition at the working temperature of the furnace and subsequent acid washing to remove free alkali.

The possibility of employing porous Alundum thimbles for filtration also received attention, but samples obtained were fragile or tended to clog easily, and the additional washing required to obtain complete removal of decomposition products was considered excessive.

**Table II**

**CARBON RESULTS (%) ON SAMPLES PREPARED IN VARIOUS WAYS FROM THREE ADJACENT PIECES OF THE SAME INGOT MOULD**

| Operator | Sample Preparation | Inside of Mould | | | Outside of Mould | | |
|---|---|---|---|---|---|---|---|
| | | T.C. | G.C. | C.C. | T.C. | G.C. | C.C. |
| (1) | Machine-cut solid pieces, $\frac{1}{8} \times \frac{1}{8} \times \frac{1}{2}$–1 in. long | 3·96<br>3·96 | 3·26<br>3·34 | 0·70<br>0·62 | 3·92<br>3·96 | 3·28<br>3·32 | 0·64<br>0·64 |
| (1) | 1-in. drill at 9 r.p.m. through $\frac{1}{4}$-in. thick slice. Proportionate weights after sieving on a 40-mesh sieve: Inside, 70·5 % retained on 40 mesh; outside, 73·1% retained on 40 mesh | 3·78<br>3·78 | 2·98<br>2·90 | 0·80<br>0·88 | 3·80<br>3·78 | 3·08<br>3·08 | 0·72<br>0·70 |
| (1) | 1-in. drill at 9 r.p.m. into solid block. Proportionate weighing: Inside, 85·4% retained on 40 mesh; outside, 68·4% retained on 40 mesh | 3·96 | 3·30 | 0·66 | 3·98 | 3·24 | 0·74 |
| (1) | 1-in. drill at 260 r.p.m. into solid block. Proportionate weighing: Inside, 52·0% retained on 40 mesh; outside, 56·8% retained on 40 mesh | 3·60 | 2·94 | 0·66 | 3·74 | 3·08 | 0·66 |
| (2) | Hacksawn solid pieces, about $\frac{1}{4} \times \frac{1}{4} \times \frac{1}{4}$ in. | 3·85 | 3·29 | 0·56 | 3·78 | 3·24 | 0·54 |
| (2) | $\frac{1}{4}$-in. drill at 50 r.p.m. | 3·82 | 3·19 | 0·63 | 3·75 | 3·10 | 0·65 |
| (3) | Hacksawn solid pieces, $\frac{1}{8} \times \frac{1}{8} \times \frac{1}{2}$ in. | 4·00<br>4·01<br>4·01<br>4·04<br>4·00<br>4·00 | 3·40<br>3·40<br>3·44<br>3·43<br>3·40<br>3·40 | 0·60<br>0·61<br>0·57<br>0·61<br>0·63<br>0·60 | | | |
| (3) | $\frac{1}{16}$-in. drill at 60 r.p.m., all sample from each hole collected and used for single determinations | 3·88<br>3·90<br>3·91<br>3·93<br>3·92<br>3·91<br>3·88 | 3·23<br>3·23<br>3·28<br>3·27<br>3·27<br>3·22<br>3·20 | 0·65<br>0·67<br>0·63<br>0·66<br>0·65<br>0·69<br>0·68 | | | |
| (3) | $\frac{1}{4}$-in. drill at 60 r.p.m., all sample from each hole collected and used for single determinations | 3·95<br>3·95<br>3·96 | | | 3·93<br>3·86<br>3·84 | | |
| (3) | Chippings taken with a pneumatic chisel | 3·94<br>3·92 | | | 3·85<br>3·85 | | |

During the investigations the value of hydrofluoric acid in facilitating decomposition of the sample and expediting subsequent filtration was confirmed and no appreciable attack on silica or porcelain crucibles could be discovered when the dilute acid solution was filtered.

It must again be emphasized that the samples referred to in Table I were carefully prepared by sieving to exclude fine and coarse particles, so providing material from which an average analytical portion could be extracted with confidence.

The method recommended in the Appendix is simple, the apparatus is readily available, and the techniques are well known. The chemical principles are fundamentally sound, and provided that sampling is carried out carefully and intelligently it is capable of producing results for combined carbon within the limits of accuracy required for most purposes.

## INFLUENCE OF SAMPLING PROCEDURE

As already mentioned, it was realized that securing a representative sample from a piece of high-carbon iron was likely to prove difficult. Westwood and Hooper,[2] for example, reported widely varying results on ingot moulds and sugar mill rolls when drillings were used but found that solid samples approximately $2 \times \frac{1}{8} \times \frac{1}{8}$ in., burnt off in oxygen either directly or after the removal of most of the iron by attack with copper potassium chloride, gave greatly improved figures. The Sub-Committee examined a number of methods of producing a sample by drilling and confirmed that a proportion of the graphitic carbon could be readily lost as fine dust during drilling. High drilling speeds and coarse graphite flakes increased the tendency to loss.

Table II indicates that solid pieces provide the highest and most consistent figures for total and graphitic carbon. Drilling at a high speed is entirely unsatisfactory even when the proportionate weighing principle is used. Drilling with a large diameter drill at very low speeds also tends to give unreliable results. Drilling with smaller diameter drills at low

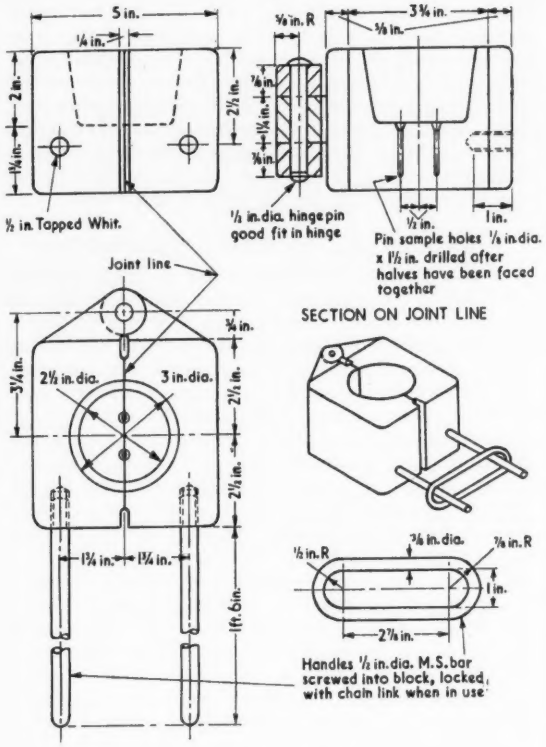


**Fig. 1—Sample mould for casting pins for the determination of total carbon by direct combustion**

speeds and using all the material from each hole as an analytical sample produces consistent results only a little lower than those from solid samples.

Further work was undertaken in an attempt to improve upon the process using a small drill. The technique finally approved was first to prepare the surface of the sample by using a $\frac{3}{4}$-in. flat-bottomed twist drill or a $\frac{3}{4}$-in. slot drill to provide a recess about $\frac{3}{8}$ in. deep. This recess was then brushed out and analytical samples were obtained by drilling into the bottom of the hole with a $\frac{1}{8}$-in. drill at not more than 25 r.p.m. It was possible to drill seven or eight $\frac{1}{8}$-in. holes in each $\frac{3}{4}$-in. recess and, by making the small holes about $\frac{3}{4}$ in. deep, approximately 1 g. of drillings was obtained from each one. The drillings were transferred to a sheet of glazed paper and the hole was carefully brushed out before the whole of the material was taken for a carbon determination.

This method of sampling was then compared with solid pieces on several casts of hematite and ingot mould iron. A further check was made against $\frac{1}{8}$-in. dia. samples cast in a special pin mould (*see* Fig. 1). At the time of sampling the molten iron a special cup-shaped mould having $\frac{1}{8}$-in. holes in the base was filled with metal. When cold the small pins were broken off and pieces of suitable length used for carbon determinations. Some results obtained from several techniques are as follows :

## Table III

**CARBON FIGURES (%) OBTAINED FROM SOLID PIECES AND FROM DRILLINGS**
**Ingot Mould Sample *MGS*/142**

| Operator | Solid Samples | | | Drillings ($\frac{1}{8}$-in. drill) | | | Drilling Speed, r.p.m. |
|---|---|---|---|---|---|---|---|
| | T.C. | G.C. | Av. C.C. by Diff. | T.C. | G.C. | Av. C.C. by Diff. | |
| A | 3·98 | 3·35 | | 3·85 | 3·16 | | 15 |
| | 3·95 | 3·39 | | 3·89 | 3·19 | | |
| | 3·93 | 3·33 | | | 3·11 | | |
| | 3·90 | 3·30 | 0·60 | | 3·16 | 0·71 | |
| | | | | 3·82 | 3·27 | | |
| | | | | 3·86 | 3·29 | | |
| | | | | | 3·22 | | |
| | | | | | 3·22 | 0·59 | |
| B | | | | 3·86 | 3·35 | | 25 |
| | | | | 3·85 | 3·30 | | |
| | | | | | 3·35 | | |
| | | | | | 3·30 | 0·53 | |
| | | | | 3·85 | 3·38 | | |
| | | | | 3·87 | 3·37 | | |
| | | | | | 3·35 | | |
| | | | | | 3·32 | 0·51 | |
| C | 4·03 | 3·43 | | 3·96 | 3·21 | | 23 |
| | 4·06 | 3·33 | | 3·93 | 3·24 | | |
| | 4·06 | 3·37 | 0·66 | 3·98 | 3·25 | 0·73 | |
| | | | | 3·98 | 3·21 | | |
| | | | | 3·99 | 3·18 | | |
| | | | | 3·96 | 3·26 | 0·76 | |
| D | 3·96 | 3·33 | | | | | |
| | 3·98 | 3·35 | | | | | |
| | 3·98 | 3·32 | | | | | |
| | 3·92 | 3·33 | | | | | |
| | 3·94 | | | | | | |
| | 3·98 | | 0·63 | | | | |
| E | 3·82 | 3·30 | | 3·82 | 3·16 | | 25 |
| | 3·89 | 3·33 | | 3·82 | 3·20 | | |
| | 3·83 | 3·28 | | | 3·26 | | |
| | 3·89 | 3·29 | 0·56 | | 3·20 | 0·62 | |
| | | | | 3·80 | 3·18 | | |
| | | | | 3·80 | 3·18 | | |
| | | | | 3·78 | 3·18 | | |
| | | | | | 3·26 | | |
| | | | | | 3·17 | 0·60 | |
| F | 4·01 | 3·38 | | 3·90 | 3·28 | | 25 |
| | 4·09 | 3·44 | | 3·90 | 3·30 | | |
| | 4·03 | 3·33 | | 3·93 | 3·28 | | |
| | 4·04 | 3·32 | | 3·88 | 3·28 | 0·62 | |
| | 4·03 | 3·37 | | 3·89 | 3·26 | | |
| | 4·03 | 3·41 | | 3·90 | 3·27 | | |
| | 4·02 | 3·41 | 0·65 | 3·91 | 3·28 | | |
| | | | | 3·90 | 3·25 | 0·63 | |
| G | 3·98 | 3·28 | | 3·92 | 3·33 | | 20 |
| | 3·96 | 3·32 | | 3·92 | 3·29 | | |
| | 3·97 | 3·27 | | 3·97 | | | |
| | 3·92 | 3·36 | | 3·93 | | 0·62 | |
| | 3·99 | | | 3·93 | 3·19 | | |
| | 3·98 | | 0·66 | 3·88 | 3·23 | | |
| | | | | 3·86 | | | |
| | | | | 3·92 | | 0·69 | |
| H | 4·02 | 3·58 | | 3·98 | 3·29 | | 25 |
| | 4·14 | 3·49 | 0·55 | 3·97 | 3·36 | | |
| | | | | 3·90 | 3·33 | | |
| | | | | 3·96 | 3·31 | 0·63 | |
| | | | | 3·92 | 3·14 | | |
| | | | | 3·90 | 3·10 | | |
| | | | | 3·94 | 3·17 | | |
| | | | | | 3·29 | 0·74 | |
| Averages | 3·98 | 3·36 | 0·62 | 3·89 | 3·25 | 0·64 | |

*Total Carbon*, %

| Material | ¼-in. Pins from Pin Mould | Sawn Samples, ¼ × ¼ × ¼ in. | Drillings: ¼-in. Drill at 20 r.p.m. |
|---|---|---|---|
| Hematite | 4·57, 4·57 | 4·52, 4·50 | 4·44, 4·45, 4·48 |
| Hematite | 4·42, 4·43 | 4·36, 4·38 | 4·36, 4·35 |
| Ingot mould | 3·97, 3·97 | 3·95 | ... |

These results show that sawn samples provide figures approaching very closely to those from the cast pin samples and although those from drilled samples tend to be a little lower they were sufficiently satisfactory to merit a full-scale trial.

Suitable sample blocks were supplied to members of the Sub-Committee from a used ingot mould of 4-in. wall thickness. The mould was broken and a piece from just above the centre-line was selected. The outside and inside faces were machined off, and from the remainder 12 adjacent test pieces were cut, each $1\frac{3}{4} \times 1\frac{1}{8} \times 1\frac{1}{8}$ in. Two $\frac{3}{4}$-in. flat-bottomed holes were drilled in each test block to provide recesses for drilling $\frac{1}{8}$-in. sample holes. Samples were prepared by individual members and their results are shown in Table III. For solid samples the total and graphitic carbons were grouped together and averaged to give an overall combined-carbon figure by difference. A similar procedure was followed with drilling, the results on the two $\frac{3}{4}$-in. holes being kept separate.

Determinations of combined and graphitic carbon on sample *MGS*/142 by the Donaldson technique modified along lines suggested earlier in this report were made, using solid samples. The results were :

| Combined Carbon, % | Graphitic Carbon, % | Total Carbon (By Addition), % |
|---|---|---|
| 0·61 | 3·40 | 4·01 |
| 0·53 | 3·42 | 3·95 |

It will be seen from Table III that both total- and graphitic-carbon results obtained from solid test pieces are about 0·1% higher than those from carefully prepared drillings. It is believed that this is partly due to the loss of a small amount of graphite which cannot be removed from the $\frac{1}{8}$-in. hole and from the twist of the drill. Preparing samples with an $\frac{1}{8}$-in. drill at low speeds is a slow operation and as the hole becomes deeper the grinding action between the drill and the iron particles at the bottom of the hole increases.

Sampling difficulties with comparatively large masses of high-carbon iron are clearly demonstrated. Each analyst was able to obtain reasonably reproducible figures in his own laboratory, using the particular sample block provided, but it is evident that some definite variation existed between blocks.

Also, whilst there is very little difference in reproducibility between the results for total and graphitic carbon obtained from solid and drilled samples, the spread of the calculated figures for combined carbon is much greater in the case of drillings. In spite of this the overall averages derived from the results are reasonably close, *viz.*, 0·62% from solid samples and 0·65% from drillings. This may also be attributed to heterogeneity of the sample, the difference in composition of individual portions being somewhat evened out when a large number of analyses are made.

These observations suggest that all the sampling methods examined can be relied upon to give the composition of the material at the sampling point only and that results obtained at any one such position must not be taken to represent the true average analysis of the whole. The problem of sampling metallurgical materials has been considered by the British Standards Institution and recommendations have been made.[6] The specific aspect of sampling cast iron is being examined by the Methods of Analysis Committee of the British Cast Iron Research Association and will shortly be the subject of a report.

## HOLLOW-MILL SAMPLING TECHNIQUE

Whilst the Sub-Committee was convinced of the necessity to use solid samples to obtain accurate and reproducible carbon figures with high-carbon irons, the preparation of this type of specimen by cutting with a hacksaw was not always convenient or easy, particularly where samples were required from a large piece of iron. A search was therefore made for a mechanical means of sample preparation and it was found that hollow mills[7] provided a simple method of obtaining test pieces of suitable size and weight. These mills, which are made in several sizes, can be fitted with an attachment, *e.g.*, a taper shank, and used with an ordinary drilling machine to give cylindrical samples of various diameters. For example the $\frac{1}{8}$-in. dia. mill drills a $\frac{5}{8}$-in. dia. hole, leaving a pencil-shaped piece of metal $\frac{1}{8}$ in. dia. standing in the centre of the hole. This pin can be broken out, and, as a piece $\frac{3}{4}$–1 in. long weighs about 1 g., it is of ideal size and shape for direct combustion in oxygen. The pins also dissolve readily in dilute nitric acid and may be used with equal success in the determination of graphitic carbon. Shorter specimens of $\frac{3}{16}$ in. dia. have also been employed; for total-carbon determina-

### Table IV

**DETERMINATION OF TOTAL AND GRAPHITIC CARBON USING HOLLOW-MILL SAMPLES**

| Sample | ¼-in. Hollow Mill | |
|---|---|---|
| | Total Carbon, % | Graphitic Carbon, % |
| **Ingot mould:** | | |
| Top section | 4·08, 4·08, 4·07 | |
| Middle section | 3·96, 3·96, 3·98* | |
| Bottom section | 3·96, 3·95† | 3·32, 3·34 |
| **Slag ladle 3¾ in. thick:** | | |
| Inside (¼ in. from edge) | 3·65, 3·64 | 3·05, 3·06 |
| Centre | 3·68, 3·71 | 3·27, 3·28 |
| Outside (¼ in. from edge) | 3·70, 3·71 | 3·17, 3·17 |
| **Slag ladle 2⅜ in. thick:** | | |
| Inside | 3·85, 3·85 | 3·15, 3·13 |
| Centre | 3·79, 3·78 | 3·09, 3·12 |
| Outside | 3·78, 3·82 | 3·15, 3·15 |
| **Hematite pig iron:** | | |
| A | 4·15, 4·18, 4·10 | |
| B | 4·25, 4·31, 4·29 | |
| C | 4·61, 4·59, 4·52‡ | |

* ½-in. Hollow mill, 3·98, 4·00 %
† Hacksawn samples, 3·97, 3·97%
‡ ½-in. Hollow mill, 4·54, 4·52%

tions, these require a longer preheating time than those of $\frac{1}{8}$ in. dia.

It has been shown (*see* Table II and p. 84) that sawn solid pieces gave consistently higher carbon figures than drillings prepared with $\frac{3}{16}$ or $\frac{1}{8}$-in. drills at low speeds. Hollow-mill samples show the same tendency, the total-carbon contents being about 0·1% higher than those from drillings:

*Total Carbon, %*

| Material | ½-in. Hollow-Mill Pieces | Drillings: ¼-in. Drill at 25 r.p.m. |
|---|---|---|
| Blast-furnace iron | 4·44 | 4·34 |
| Blast-furnace iron | 3·77 | 3·62 |
| Ingot mould *A* | 4·09 | 3·98 |
| Ingot mould *B** | 3·97 | 3·90 |
| Ingot mould *C* | 3·84 | 3·74 |

* Total carbon of solid piece prepared with hacksaw, 3·97%

Table IV shows that good reproducibility is possible with the hollow-mill technique for both total and graphitic carbon on all the cast-iron samples. The sensitivity of the method is demonstrated by its ability to bring out small differences in carbon content over the cross-sections of the slag ladle samples. With the hematite pig irons the results are a little less consistent, particularly with the highest carbon material. This is probably accounted for by the fact that this type of iron has larger and more irregularly distributed graphite flakes than the cast irons examined.

The following results from a 4-in. thick ingot mould are considered to be very consistent when the heterogeneous nature of the material is taken into account: the reproducibility of the hollow-mill sampling method is again demonstrated:

*½-in. Hollow-Mill Samples*

| Operator | T.C., % | G.C., % |
|---|---|---|
| 1* | 3·96, 3·95 | 3·34, 3·32 |
| 2 | 3·90, 3·95, 3·96 | ... |
| 3 | 3·95, 3·99, 4·07, 4·10 | 3·24, 3·29, 3·36, 3·38 |
| 4 | 4·01, 4·07 | ... |
| 5 | 4·01, 3·99, 4·05, 4·05 | 3·33, 3·31, 3·35, 3·34 |
| 6 | 3·97, 3·94, 3·98 | ... |

* Total carbon from hacksawn samples: 3·97, 3·97%

## CONCLUSIONS

In the Sub-Committee's view the question of sampling is of paramount importance in any problem involving the determination of carbon in cast iron. After a very large amount of research, both co-operative and in individual laboratories on behalf of members' own companies, the considered opinion is that the use of solid samples offers the best means of obtaining reproducible figures with the least chance of loss of graphite. This suggestion does not obviate the difficulties of obtaining analytical samples representative of a casting as a whole, for which there does not appear to be any method available at present. In an ingot mould, for example, a random distribution of coarse graphite flakes is almost inevitable, and when any analyses for carbon are quoted the actual position of the sampling point should be stated.

Drilling, even under the most carefully controlled conditions, usually leads to a small but significant loss of carbon, particularly with high-carbon, coarse-graphite irons. When drilling has to be employed the most suitable procedure appears to be an $\frac{1}{8}$-in. drill at not more than 25 r.p.m. to give a sample weighing about 1 g., the whole of which is used for a single determination. Separating a drilled sample into fractions by sieving and using the correct proportions of each of the particle sizes for carbon determinations seems to be less satisfactory. Drillings obtained by conventional methods at moderate or high speeds are quite untrustworthy.

When solid pieces cannot be obtained easily, quickly, and conveniently by sawing, an $\frac{1}{2}$-in. hollow mill is recommended. Small cylindrical pins can be produced with this tool from almost any position which can be sampled by drilling.

After carefully assessing the relative merits of the direct and indirect methods available for the determination of combined carbon in the light of present knowledge, the difference method detailed in the Appendix is recommended as the most satisfactory yet developed. Its weakest point is that it does not provide a direct measure of the desired constituent, but if operated carefully it is a reasonably accurate and reproducible procedure employing apparatus and reagents in everyday use in metallurgical laboratories.

The Donaldson method requires special apparatus and does not produce accurate results, since the mixtures used for solution and oxidation of the sample are liable to attack graphite. Modifications examined by the Sub-Committee gave improved performance at the expense of increased operating time and the results did not justify further investigation.

## Acknowledgments

The Sub-Committee acknowledges its indebtedness to Mr. A. W. Reed (Consett Iron Co., Ltd.) for the recommendation of hollow-mill sampling and for much of the work carried out with this technique; also to Thermal Syndicate, Ltd., for the supply of special crucibles.

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# APPENDIX

## Recommended Procedure for the Determination of Combined Carbon in Iron

Total and graphitic carbon are determined separately and the combined carbon is obtained by difference. The method gives results reproducible to $\pm 0{\cdot}05\%$ for a range of plain and alloy irons containing up to $4\frac{1}{2}\%$ of total carbon.

### Total Carbon

*Apparatus*—Combustion furnace and accessories as described in B.S. 1121: Part 11: 1948.

*Sampling*—A hacksawn or hollow-milled solid

sample (*see* p. 84) taken from a predetermined position in the casting, or a pin prepared from the liquid metal (*see* p. 83) is required.

*Procedure*—The operating conditions described in B.S. 1121: Part 11: 1948, Section 4 (i), are satisfactory if a furnace temperature of 1150° C. and a preheating time of 3–5 min. are employed. An accurately weighed sample of about 1 g. should be used.

**Graphitic Carbon**

*Apparatus*—Combustion furnace and accessories as described in B.S. 1121: Part 11: 1948. Suction flask fitted with a rubber collar to hold a filtering crucible. The filtration of graphite is preferably carried out through a pad of good-quality asbestos supported on a silica grid, sintered in a silica crucible at least 3 in. high and of suitable diameter for direct insertion into the combustion furnace.

*Reagents*—Nitric acid (2: 3), sodium hydroxide (1%), hydrochloric acid (1: 19).

*Sampling*—As for total carbon. The sample should be selected from an adjacent position, or may be a portion of the sample already obtained.

*Procedure*—An accurately weighed sample of about 1 g. is dissolved in 60 ml. of nitric acid (2: 3) by warming gently and 1 ml. of hydrofluoric acid is added. The solution is boiled in a covered beaker for 5 min. and then digested just below boiling point for a further 45 min. (If Cr is present the period of digestion should be at least 1 hr.; the volume of the solution must be kept above 40 ml., if necessary by additions of nitric acid (2: 3)).

Finally, boil for 5 min. and filter through a silica-grid filtering crucible with asbestos pad,* using gentle suction. Wash three times with hot water, three times with hot sodium hydroxide solution (1%), three times with hydrochloric acid (1: 19), and finally six times with hot water. Dry the precipitate as far as possible by suction.

Dry the crucible and contents for 1 hr. at 105–110° C. and ignite in the combustion furnace as described in B.S. 1121: Part 11: 1948, Section 4 (i). No flux is required.

**Combined Carbon**

The total and graphitic carbon are calculated as percentages on the sample weights taken and the combined carbon is obtained by difference.

* The asbestos used for filtration should be free from long, coarse fibres and must be ignited in air or oxygen at the operating temperature before use. It should be packed loosely so that carbonaceous matter can be removed readily. It should be cooled and washed well with hydrochloric acid (1: 19) and hot water after ignition, to remove free alkali and also part of the fine fibres which otherwise tend to make filtration very slow. The blank on the asbestos should be determined.

## LETTER TO THE EDITOR

### Oxalic Acid Dihydrate as a Source of Low Water-Vapour Partial Pressure

Water-vapour/hydrogen mixtures are of value in the study of reactions of interest in steelmaking, but an ordinary water saturator requires a thermostat bath operated below room temperature to yield water-vapour partial pressures of less than about 15 mm. Hg.

This note draws attention to the suitability of oxalic acid dihydrate as a source of low water-vapour partial pressures, since its water-vapour pressure ranges from about 1·5 mm. at 18° C. to 15 mm. at 50° C. In addition the reliability of Baxter and Lansing's* data is confirmed.

Baxter and Lansing's results were checked by passing hydrogen, dried by means of anhydrous magnesium perchlorate (Anhydrone) through two tubes each 30 cm. long × 6 cm. dia., followed by a **U**-tube, 75 cm. × 1 cm., all filled with the mixture recommended by Baxter and Lansing, *viz.*, 90% oxalic acid dihydrate, 10% of the anhydrous acid, and a few glass beads. The tubes were immersed in a well-stirred thermostat bath. The water in the emergent hydrogen was determined by collection in weighing tubes filled with Anhydrone, and the volume of the hydrogen was recorded on a calibrated gas meter.

Preliminary work with an uncalibrated thermal conductivity gas-analysis unit showed that the water content obtained with the above system was independent of flow rate up to 20 litres/hr., which was the maximum rate studied. When the temperature of the hydrate had been raised by 10° C., the analysis unit showed that the system reached equilibrium again within 10 min.

The actual water-vapour pressures obtained are as follows:

*Aqueous Pressure, p(mm.), over Oxalic Acid Dihydrate*

| t° C. | Present Results | Baxter and Lansing |
|---|---|---|
| 20·0 | 1·85 | 1·82 |
| 31·1 | 4·13 | 4·18 |
| 40·4 | 8·15 | 8·10 |
| 45·05 | 11·15 | 11·15 |
| 49·8 | 15·20 | 15·30 |

Also shown are the pressures calculated from Baxter and Lansing's equation:

$$\text{Log}_{10}p(\text{mm.}) = 18{\cdot}053 - 9661/(T + 250) \quad (T \text{ in } ^\circ\text{K.})$$

The excellent agreement confirms that Baxter and Lansing's equation can be used with a high degree of confidence.

This technique was used by one of the authors in a recent study† of the free energy of formation of magnesium phosphate.

The work described was carried out while the authors were in receipt of bursaries from the British Iron and Steel Research Association, and the interest of Dr. A. J. E. Welch was warmly appreciated.

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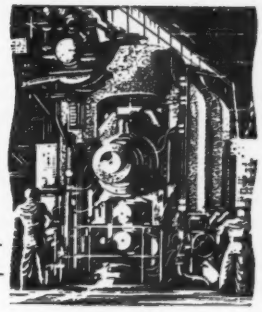
* G. P. Baxter and J. E. Lansing, *J. Amer. Chem. Soc.*, 1920, vol. 42, p. 419.

† J. B. Bookey, *J. Iron Steel Inst.*, 1952, vol. 172, pp. 66–68.

IRON AND STEELWORKS ENGINEERING

THE IRON AND STEEL ENGINEERS GROUP



# THE IRON AND STEEL ENGINEERS GROUP

## *REPORT OF THE EIGHTEENTH MEETING*

THE EIGHTEENTH MEETING OF THE IRON AND STEEL ENGINEERS GROUP of The Iron and Steel Institute was held at 4, Grosvenor Gardens, London, S.W.1, on Thursday, 17th April, 1952. Mr. C. H. T. WILLIAMS (The Park Gate Iron and Steel Co., Ltd.), Chairman of the Group, occupied the Chair.

THE MORNING SESSION was occupied by the presentation and discussion of a paper on "Supply and Use of Hydraulic Power at Appleby-Frodingham," by Mr. L. N. LLOYD of Appleby-Frodingham Steel Company.

THE AFTERNOON SESSION was devoted to the presentation and discussion of a paper by Mr. C. G. EVANS and Mr. P. L. FAIRFIELD of the Harland Engineering Co., Ltd., on "Pump Design and Applications in Iron and Steel Works."

*PROCEEDINGS OF THE MORNING SESSION:* 10.30 A.M. to 12.45 P.M.

### Discussion on the Paper—

### SUPPLY AND USE OF HYDRAULIC POWER AT APPLEBY-FRODINGHAM*

Mr. **L. N. Lloyd** (Appleby-Frodingham Steel Co.) presented his paper. He pointed out that in the paper as printed, the rates of flow in the inset scale on Fig. 2 should be 1000 and 2000 gal./min. In the table in the second column of p. 273, the weight of water in the main between the accumulator and the shear branch should be 2·8 tons. The second paragraph of the section headed "Relays and Jacks for Control Valves" on p. 280 should begin "The 10-ft. mill skid gear, turnover arms, etc., are operated by a thrustor-actuated battery of 15 double-acting 2-in. pilot-controlled valves." In the table in the first column of p. 284, the second line should read "Outlet area of nozzle..... $\frac{1}{16}$ in. × $\frac{1}{2}$ in." The cutting angle given in line 5 of the first column of p. 286 should be 1 in 20.

Mr. **J. G. Frith** (Davy and United Engineering Co., Ltd.): In connection with the graph showing the acceleration-head formula, Mr. Lloyd said that change of velocity could be taken instead of change of flow. If this were done, the formula would be reduced to

$$P = \frac{LV}{74 \cdot 3X}$$

where $P$ = acceleration-head pressure
$L$ = length of pipe, ft.
$V$ = change of velocity, ft./sec.
$X$ = time for the change, sec.

With 100 ft. of pipe, $P = \frac{4V}{3X}$.

$P$ could also be the deceleration-head pressure if a valve were being closed in a given time with a given velocity.

The deceleration-head pressure must, however, be added to the line pressure (*see* Table II, where the nominal 750 rises to 1000 lb. at the finish of the cut). That shock pressure is, according to this formula, independent of both line pressure and pipe size. By dealing with a mass of water and the change of velocity, the decelerating force is given in lb./sq. in., which cancels out the area of the pipe. Shock loading is therefore independent of line pressure, and must be relatively greater in the case of small line pressure than of large.

In his description of the surge tanks, Mr. Lloyd has given an excellent way of getting over the trouble due to a long return main. This is the converse of the accumulator, as the surge tank takes the peak load, and the long main runs steadily throughout the whole of its time, like an accumulator pump, allowing the water to take its own time down the mains.

The proportion of soluble oil to water is given in Appendix II as 5 parts in 100,000, which is said to give good results in reducing friction and eliminating corrosion. For closed systems the normal recommendation is a ratio of 1–5%. No doubt that could not be used by Appleby-Frodingham, who require 120 gal./min. of make-up water; to put a high percentage of soluble oil

* *J. Iron Steel Inst.*, 1952, vol. 170, pp. 271–287.

in, only to lose it down the drain, would not be economical. But it is surprising that a ratio of 1 part in 20,000 can have any appreciable result. Would it be economical to draw the expendible water for descaling and washing from a separate system and keep the main hydraulic system as a closed circuit, working the shears, manipulators, etc., only? It would then be possible to use a higher ratio of soluble oil to water without loss.

As regards balance cylinders, it is better to have a separate accumulator, because of the varying pressures in a service accumulator.

The steam-operated intensifier as used on the slab shears is, unfortunately, falling out of general favour, chiefly because of the difficulties of raising steam and the cost of fuel. It is, however, a very flexible method of operation, and I am glad to hear that the Appleby-Frodingham unit works well.

The presence of sludge in water, as mentioned in Appendix II, can give rise to very real problems. Some years ago, I investigated a small press driven by a direct pump working on water, which for some years had been in the London area, where it had been lubricated with tallow or fat. During the war, the plant was moved to Ross-on-Wye, and, after a few weeks, there were complaints that it would not work properly. It was found that when working in London on hard water, the calcium in the water had reacted on the grease and formed a deposit inside the cylinder. However, at Ross-on-Wye the water there started dissolving the deposit and thus gummed up all the valves in the pump. We found a deposit of white slime at least $\frac{1}{2}$ in. thick on the cylinder walls, the removal of which completely cured the trouble.

Mr. **L. N. Lloyd**: Mr. Frith is not strictly correct in saying that, according to the acceleration-head formula converted to a velocity basis, shock pressure is independent of pipe size, since for any specific change of rate of flow the change of velocity will be greater in a small pipe than a large one.

Mr. Frith, like me, seems to be moved by the massive nature of steelworks plant and the aura of drama that surrounds its operation. The slab shear, with its associated steam-operated intensifier, is a machine of which the Davy and United Engineering Co. may well be proud, since it has given many years of service.

In regard to steam supply, this, as installed, was from melting-shop waste-heat boilers, and so was an economical proposition.

In regard to the use of a separate pump for descaling, we have two pumps lying idle all the time. They are changed over from time to time, and we did consider putting one of those pumps on to descaling only, but since they are large, it would not be economical to do so. It is cheaper to use make-up water consisting of a mixture of treated and untreated water with a soluble oil addition than to run an extra pump with untreated water only. The water from the sprays, in common with the roll and roll-bearing cooling water, is recovered, filtered, and re-used for cooling, but the cost of treatment is lost.

I should like my colleague, Mr. Jones, to speak on the subject of soluble oil.

Mr. **H. Jones** (Appleby-Frodingham Steel Co.): On the question of the small additions of soluble oil, Mr. Frith indicated part of the reason for their effectiveness when he mentioned the accumulation of grease found inside the cylinder of the press moved from London to Ross-on-Wye.

Although the concentration of soluble oil in the make-up water at the Appleby steelworks is as low as 1 part in 20,000, it is quite adequate for the purposes for which it is put in. This is partly due to a constant deposition of the oil on the cylinder walls, ram heads, etc., until all the surfaces are covered by a layer, probably adsorbed, of lubricating material. When it is realized that about 1,200,000 gal. of water are added to the system each week, it will be appreciated that the cost of attempting to maintain anything like a 5% concentration would be prohibitive.

The plant maintenance engineers are all emphatic about the usefulness of soluble oil, claiming that not only does it prevent sticking, reduce wear, and prolong the life of the packing, but that it also reduces by an appreciable amount the effort necessary to operate the heavier valves.

All the advantages derived from these additions cannot be attributed solely to the lubricating properties of the oil as such; some must be due to the enhanced lubricity of the water itself. This improvement is due to the increased ability of the water to wet surfaces, brought about by the addition of the soluble oil.

Mr. **J. G. Frith**: What were the results of hard-facing the relief valves with tungsten carbide?

Mr. **L. N. Lloyd**: The valve seating that we had under test was hard-faced with Ardite. We are now hard-facing a valve with Stellite, but that has not yet gone into the system. We had good results from the first Ardite valve seating, and I recommend it.

Our first step was to fit all valves with stainless-steel internals, which have proved most successful in considerably prolonging the life of the valves. The accumulator-operated relief valves were working under very severe conditions, and stainless steel was not adequate, but the hard-facing, provided that a high-velocity jet does not directly impinge on the face, does give a much prolonged life. It is most important to keep that valve in good condition, because a leak involves much loss of horsepower.

Mr. **F. H. Towler** (Towler Brothers, Ltd.): The hydraulic press, as a press, has a mechanical efficiency of over 90%, but the overall efficiency of an accumulator system is about 20%. This is because a hydraulic press is seldom, if ever, operated at maximum force throughout the working stroke. A 600-ton shear consumes the same amount of hydraulic pressure, whether it is shearing a billet or a halfpenny, *i.e.*, the accumulator has to be pumped up at full pressure, whatever work has been done at the shear.

In a paper delivered to the Institution of Mechanical Engineers* in 1945 I showed that a saving of 75% in power consumption could be made by converting to the direct oil-hydraulic system. This has since been amply proved by the conversion of several small hydraulic plants, the hydraulic accumulator being discarded.

Saving in power is by no means the only advantage to be obtained by such conversion. Long pipelines, with possible bursts due to frost or to shock, are excluded, and corrosion is eliminated by using oil as the hydraulic medium; with water, the press works some of the time, but corrosion, which did most of the damage to valves and packings, works all the time.

Another advantage of the direct system is ease of control and greater precision. Valves are small and can be operated by a small hand-lever; there is no need to have a hydraulic engine to operate the valve. They use much higher pressures (4500 and often 7000 lb./sq. in.), which means greater efficiency, smaller press rams, etc. Shock pressures become insignificant at these higher pressures.

Mr. Lloyd's figure of 20 lb./sq. in. for accumulator-

* *Proc. Inst. Mech. Eng.*, 1946, vol. 154, pp. 178–189.

gland friction is rather low; perhaps it is due to water-film lubrication. One has to choose between 10% leakage and 1% friction, or *vice versa*, but the leakage remains.

What is the total leakage in gal./hr. of the whole system? What is the cost of hydraulic pressure water at the press after taking account of this leakage? And what is the cost of maintenance per gallon of pressure water actually used?

The 18 in. × 54 in. slab shear is probably the most efficient machine in the whole plant, because it is operated by a steam intensifier; the steam is used expansively as the shearing force diminishes towards the end of the stroke. There might be a return to the direct steam-hydraulic system if the heat in the steam could be conserved and produced economically by waste heat from the furnaces and gas engines.

Pressure surges in the pipe lines might be measured more accurately by electronic means. A damped pressure gauge will not record momentary peak pressures due to shock. I would be happy to collaborate with Mr. Lloyd in a further investigation of pressure surges in these long pipelines.

Mr. **L. N. Lloyd**: Mr. Towler has made a very good case for the operation of large hydraulic machines by individual pumps, but the choice between individually driven units and units driven off a hydraulic-supply grid depends on the applications that it has to serve. In the Appleby steelworks, in addition to the large users, such as the melting-shop tilting cylinders, the return cylinders for the slab shears, and large plate-shearing machines, there are many smaller users, such as rolling-mill manipulators, cooling-bank manipulators and turn-over arms, throw-off tables, furnace-door operators, etc. There are also rolling-mill balance cylinders and descaling sprays. Where such a diverse use is made of hydraulic power, operation from a hydraulic power grid is essential. Furthermore, the larger the number of users, the greater is the diversity factor, and consequently the overall efficiency.

Mr. Towler's remark about shearing a billet or a half-penny is not strictly correct. In a plate mill, the shearing machine has to be massive enough to shear the thickest plate within the range of the mill, and this mass has to be accelerated, whether the plant is operated by a unit pump or from a grid supply. The pressure supplied by a grid system is constant, and the whole of this pressure is not required for mass acceleration and cutting when dealing with a thin plate, but it is not entirely lost, as the excess pressure is used in reducing the time of the cutting cycle. On the other hand, the unit pump machine runs at a fixed speed.

The tendency today is to use geared electric motors for driving heavy shearing machines and operating mill manipulators, but the motor-starting gear, the reduction-gear train, and the means for converting rotary to straight-line motion, where this is required, are costly compared with a simple hydraulic cylinder. In machine tools, however, the tendency now is to dispense with mechanical transmissions, and to use hydraulic rams for table motions, feeds, etc. The saving is most marked where complicated motions have to be transmitted.

The use of soluble oil in the hydraulic water and of stainless steel for valve internals has greatly reduced maintenance. Mr. Jones spoke of the use of soluble oil, the result of which was remarkable. Previously, the rams became scored through leaky glands; once scoring starts, deterioration progresses at an accelerating rate, since it is difficult to keep the glands tight. The small amount of lubrication provided by the soluble oil prolonged the life of the packing and eliminated ram scoring.

The relative costs of maintenance favour hydraulic equipment, so that with modern centrifugal pumps of about 70% efficiency and modern materials, there is still much to be said for the hydraulic grid system.

We have used strain gauges for measuring roll-neck bearing pressure, but the Duddell oscillograph is perhaps better, since a number of remote observations can be recorded simultaneously on a photo film; for pressure observations, an attachment is available whose electrical properties vary with pressure. However, both these methods are costly.

As previously mentioned, we found that it would be uneconomical to use one of the existing stand-by pumps for operating the rolling-mill washing sprays.

The overall efficiency of the pump on its economic load is 56·6%, and, assuming an electrical efficiency of 93%, it is reduced to 55·2%. With electricity at ¾*d.* a unit, the cost of power only comes to 1·05*d.* per horse-power hour of hydraulic water in the main, *i.e.*, the horsepower that one has available. The cost of the water itself was about 9*d.* per 1000 gal. for power, and the all-in cost of the hydraulic system, including pump attendance and maintenance of all the hydraulic plant, is 12·675*d.* per 1000 gal. of water.

In regard to Mr. Towler's remarks on gland friction, further observations at the plate mill accumulator show that there is no gland leak, and the differential pressure to keep the ram slowly rising is 25 lb./sq. in. This mainly represents gland friction, and we attribute this low figure, like Mr. Jones, to the use of soluble oil.

Mr. **J. A. Addison** (Duncan Stewart and Co., Ltd.): The general accumulator supplying all services, as at Appleby-Frodingham, is not ideal. A better scheme, adopted in many modern installations, is to have separate accumulators for service and balance duties. This ensures that the pressure on the balance rams is practically constant and unaffected by sudden service demands.

An added advantage is that when air-loaded accumulators are used, the pressures may be readily adjusted independently in each system to give the best operating results.

Since the consumption of fluid from the balance accumulator is negligible if all balance-ram packings are well maintained, it should be unnecessary to install a separate pump, this system being topped up with fluid by opening an automatically operated bleeding valve in the service system.

Mr. **C. G. Evans** (Harland Engineering Co., Ltd.): Mr. Lloyd has shown a gauge for measuring balance-disc wear. The modern pump incorporates a wear indicator (dial or straight pointer) as an integral part of the pump, and such provision is not now left to the ingenuity of the steelworks engineer.

The positioning of the impellers in a centrifugal pump is critical as regards its capacity to deliver the required quantity, and if the balance disc is allowed to wear unduly, the impellers will get out of step with the guide ports; it may then be necessary to have a third pump to make up the quantity. Maintenance of the balance disc is very important.

Mr. Lloyd mentioned that the phosphor-bronze impellers in a five-stage pump, at 750 lb./sq. in., became badly bent at the vane tips. This is surprising, since 750 lb./sq. in. on a five-stage pump is only 350 ft. per stage, which is standard for bronze. Stainless steel is certainly stronger than bronze and is more erosion-resistant, but as a standard, stainless steel is not normally used until 500 ft. per stage is reached, or unless severe suction conditions are expected. Good-quality bronze is suitable at 350 ft. There must be some other reason to account for the phenomena referred to by Mr. Lloyd,

such as prolonged operation at much reduced flow where severe churning would occur.

Mr. Lloyd improved serious erosion of the by-pass valve by hard-facing stainless-steel parts. Our experience with Stellite is very good. We have used it for sleeves with sand or abrasive-laden water, and we are satisfied that, in regard to gland wear, Stellite gives better wear-resisting properties than stainless steel.

But that valve should not do the controlling. It should be followed by a simple single- or multi-hole orifice plate to restrict the flow and break down the pressure. Such a plate is easily replaceable and is of hard abrasion-resisting alloy. Up to 600 lb./sq. in., a single hole in the plate is effective; beyond that, a whistling or screaming emanates from a single hole, so that current practice is to have eight, nine, or more holes in parallel in the plate, which largely breaks down the noise. This method is now being used extensively for high-pressure boiler-feed work, and has proved effective. For that reason, the valve makers are only breaking down a small portion in the leak-off valve, the remainder being done in an orifice.

Mr. Towler's pump is particularly useful when applied to small flows, but when quantity is needed, water is the natural medium.

Mr. **L. N. Lloyd**: All five impellers were originally made of phosphor-bronze. The first two stages were later converted to stainless steel because they wore so badly. On opening up the pumps at the time of the investigation, we found that the other stages had worn similarly, and therefore, having maintenance in the forefront of our minds, we did what we could to remove this considerable wear and tear on the impellers. It was mainly cavitation caused by the bad state of the system and possibly particles of dirt that brought about this serious wear of the remaining stages, but as maintenance men, we took direct action and fitted stainless-steel impellers to all stages. The results certainly justified this step.

The stainless-steel impellers have one disadvantage compared with phosphor-bronze, and that is the difficulty of making the actual impeller conform exactly with the design. It is a metal cast at a high temperature, and it is almost impossible to get any instrument to grind the faces of the vanes to get them to the right profile, or even to remove their roughnesses, so that a phosphor-bronze impeller is the better job from the hydrodynamic point of view.

Balance disc wear not only causes a loss of impeller throat area; the high-velocity stream impinging on the periphery of the diffusion chamber walls also causes serious turbulence loss.

I am glad to hear the confirmation of Stellite; when steelworks engineers try out things, it takes a long time to get results, since development work always has to give way to maintenance, so that a discussion like this is very helpful, because the information exchanged saves experimental time. For the same reason I was glad to hear Mr. Evans's remarks about the orifice plate for breaking down pressure beyond the relief valve. We had considered this method and, with the information given, we should be able to apply it with the minimum of experiment.

Mr. **A. H. Bennett** (Walter Somers, Ltd.): The surge tanks are placed in the roof-valley gutter and discharge by gravity into the return mains, and thence to the supply tanks for the hydraulic pumps. This arrangement creates extreme shocks in the return pipelines to get the column of stationary water suddenly on the move as soon as an exhaust valve is opened, and also limits the height of the supply tanks above the pumps.

Was the placing of these surge tanks underground ever considered? By this arrangement, all exhaust water would be virtually opened to atmosphere, and would easily drain into the tanks without shock; a motor-driven pump controlled by a float-operated switch could then be used to pump the water to the supply tanks, which could be erected without restriction at the most suitable height for the pumps.

Some years ago, we had much trouble with the return pipes when exhausting water from cylinders at 2 tons/sq. in. to the supply tank situated only 12 ft. above floor level. By constructing a surge tank in the ground under the control valves we solved the problem, and it was only necessary to have a relatively small motor-driven pump to return the water to the overhead supply tank.

I can support Mr. Lloyd's recommendation that rams should be faced with a chromium deposit to provide a hard mat surface. In our works, hydraulic accumulators with cast-iron rams have caused most trouble owing to leakage and short life of the packing. This material should be avoided for such rams. In one accumulator with a cast-iron ram of 14½ in. dia. × 20 ft. stroke, a new set of packing would remain tight for only three days before excessive leakage occurred. It was therefore necessary for the gland to be tightened repeatedly; the ultimate life of the packing was about three weeks, in spite of the fact that the surface of the ram was smooth and the greatest variation in diameter throughout its length was 0·003 in. The ram was replaced in November, 1945, by a new one in mild steel, the surface of which has a deposit of nickel, ground and polished. The original set of packing is still in use without leakage or attention of any kind.

On a completely closed hydraulic system it is advisable to start up with a 2% oil solution. This is more than is normally necessary, but if a plant is brand new, with tight clearances, it is as well to provide extra lubrication. After the running-in period, the amount can be reduced to 1% or even less, so that with the proper application of packings and treatment, leakages are reduced to the minimum.

From experience, I can support Mr. Frith's remarks in favour of the steam-hydraulic intensifier. It is easily controlled and flexible, and even for a large forging press only two valves—steam inlet and steam exhaust—are required to operate it; there are other valves for raising and lowering the crosshead and for anvil moving, but these do not present any difficulties. This system demands a large steam-raising plant, which must be started up well in advance of the working period and pressure maintained throughout, so that at the end of operations, a large quantity of potential energy is lying idle and stand-by losses are large. The main advantages of steam-hydraulic operation are flexibility and absence of shocks.

With power-hydraulic operation there are no stand-by losses, but much more equipment is required, and maintenance needs to be greater to keep the plant working efficiently. The pipe sizes and water velocities have to be studied, and shock-absorbing vessels are necessary to obviate trouble in the pipelines.

One trouble with centrifugal pumps is apparently maintaining the location of the impeller, which is important to obtain maximum efficiency. Has the use of a double-thrust bearing of the ball type ever been considered, or, if the speed is excessive, of the Michell thrust-block type? We have a thrust block of the latter type that has been in continuous operation for over 30 years, and, apart from burnishing the bearing surfaces at each annual overhaul, no other maintenance has been entailed.

Mr. **L. N. Lloyd**: Mr. Bennett's alternative scheme for the surge tanks is certainly very attractive, because an automatic low-pressure centrifugal pump needs little maintenance and, as he points out, its use does not restrict the height of the feed tanks at the main pumping station.

The overhead tanks actually serve another useful purpose, since they also act as reflux vessels. We have three big shears at the bottom end of the mill that are operated hydraulically, and each of them has one of these overhead tanks. They are 30 ft. long by 5 ft. dia., but the structure of a steelworks is suitable for supporting such a tank. The columns have to be strong enough to carry heavy cranes and a wide roof span, so the extra load is small, and it is just a question of the cost of getting the tanks up there. The tank is connected freely to the return main, so that if any other user nearby finds it difficult to get rid of water quickly enough, it becomes a reflux vessel and offers temporary storage for that water also.

These big shears use water at a very high rate, as much as 1000 gal./min. for brief periods. Normally the cutting time is only about 20% of the complete cycle, *i.e.*, running in and setting the plate, cutting, and running the plate off, so the reflux tank has plenty of time to get rid of its water. When cutting a scrap plate into strips for remelting, the cycle is much faster, and so the tank must have a large capacity to tide over such periods. Similarly, the underground tank that Mr. Bennett mentions would need to be large, otherwise a fairly large pump would be required to dispose of the water.

The pumps that we use do have Michell thrust bearings. Their virtue is to take the load when the pump is running up, otherwise the balance-valve disc would rub on the seat, and would have no water to lubricate it; it would be in metallic contact, and wear would be considerable. The thrust pad relieves the balance valve of that load until the pump is run up to pressure and the axial thrust of the impeller has lifted the balance valve off its seat. I am informed by pump makers that the balance valve is essential.

Mr. **W. H. Alvey** (English Steel Corp., Ltd.): We have had considerable trouble with main hydraulic control valves, similar to Fig. 11, on large forging presses operating at a working pressure of up to 3 tons/sq. in. When the pilot valve is opened to dissipate this energy, water at high velocity rushes through the small annulus between the main valve and the cage, causing rapid wear through erosion, which very soon tends to create a flow at a greater rate than the pilot valve can discharge; consequently, the high back-pressure prevents the main valve opening. This trouble was overcome by fitting a hydraulic seal in the main valve to prevent this leakage. A controlled orifice, similar to that shown on the right-hand side of Fig. 11, is used to reduce the back pressure above the main valve when the pilot valve is opened.

Hydraulic seals of the **U** leather type have also been successfully used for making high-pressure hydraulic pipe joints. With this method, excessive force is not needed when tightening up the pipe flanges, and, from our experience, the joints not only need no further attention for long periods, but some flexing of the joints can take place without leakage.

Mr. **L. N. Lloyd**: Mr. Alvey made a very interesting point about the pilot-operated valve. I shall have to ask our pipe-fitter what his experience has been with these valves, because I do not know myself, but I shall certainly suggest to the steelworks engineer this method of overcoming wear, if it exists in our works.

The idea of using a **U** leather for a pipe joint is good. All who are familiar with steelworks know that fitters have a tendency to overstrain bolts when tightening the nuts. This type of joint should reduce that tendency.

I cannot give any precise information about the life of 'Ardite' hard-facing. It is important not to let a jet of water impinge on the valve or clack seats. The fluted grooves in the guides below the valve clack were introduced by one of our engineers to give a cushioning effect during valve closure, and proved effective in this respect. Unfortunately, the flare of the fluting at the top of two of the grooves was incorrectly machined, and consequently at these points high-velocity jets impinged upon the hard-facing of the valve clack. This caused local pitting, but elsewhere the hard-facing gave promise of good results.

Mr. **S. Gibson** (Park Gate Iron and Steel Co., Ltd.): The piston heads of the tilting cylinders on the melting furnaces at Appleby-Frodingham are fitted with two Lockwood and Carlisle piston rings. The make-up water there has 1 grain of suspended matter per gal., whereas at Park Gate it has 1·3 grains. Does Mr. Lloyd experience any difficulty with ring sticking owing to the sludge content, and has he any data on the length of time between examinations?

At Park Gate, we used a similar type of piston head without success years ago; we now use the 'Lion' block-type packing.

Mr. **L. N. Lloyd**: Although there is only 1 grain of suspended matter in the Appleby water, the particle size is such that it will settle out. This may not be the case at Park Gate, especially if the suspended matter derives from water softening. Another possibility is that the soluble oil addition may react on permanent or temporary hardness and throw down the slimy deposit. There is another factor in play at Appleby; using this water for descaling is like using the blow-down valve on a boiler—it reduces the concentration of undesirable elements.

Mr. **A. P. Clark** (Dorman Long and Co., Ltd.): Some years ago, I was informed by the Appleby-Frodingham engineers that their furnace tilting-cylinder rings were examined, and expanded every 9–12 months. The life of a set of rings was 15–20 years, and only one tilting cylinder had been changed in over 20 years.

I recently asked one of the principal oil suppliers what proportion of soluble oil they would advise for a hydraulic system. Their recommendation, 1 part in 200, is rather surprising, compared with the proportion of 1 part in 20,000 that Appleby-Frodingham find satisfactory.

I was interested to learn that the alleviator in the long pressure main has now been removed. This alleviator, I understand, was installed to relieve pressure surges, largely due to the closing of the operating valves at the shears; have improvements to these valves so reduced the water hammer as to make the alleviator redundant?

Mr. **L. N. Lloyd**: The conventional alleviator, owing to its short stroke, is of only limited usefulness. The deceleration head depends on the deceleration rate, and a 4-in. dia. alleviator has so little displacement that its effect on an 8-in. main is negligible. The one at the cross-cut shears was removed because of the amount of week-end maintenance it required. It has not been missed, and I think the explanation is as follows: the accumulator, 288 ft. upstream, acts as an alleviator for the deceleration head between it and the pumps. This head accelerates the accumulator ballast upwards,

enabling the accumulator to store energy. At the cross-cut shears, the branch piping has been simplified and the ram cylinders reduced in diameter. This has reduced back pressure; consequently the apron balance cylinder responds more readily to line pressure, and so by lifting the apron acts as an alleviator while doing useful work. A third means of controlling deceleration head is by adjustment of valve-closure speed.

Mr. **W. M. Hadden** (Dorman, Long and Co., Ltd.): Mr. Lloyd described the hydraulic cylinders for the tilting furnaces as having pistons fitted with metal piston rings of the Lockwood and Carlisle design.

To the best of my knowledge, metal piston rings have only been fitted into hydraulically operated pistons for tilting furnaces and converters, but for most other steelworks hydraulic applications soft packing, either of the block or automatic type, is generally used. It is, therefore, rather difficult to understand why metal piston rings are installed in cylinders for tilting furnaces; these cannot wholly prevent the leakage of high-pressure water past the piston, as it is not practically possible to fit their bearing surfaces so as to prevent leakage. The bearing pressures per square inch between the metal surfaces are, moreover, exactly the same as the working pressure of the water, whereas, for efficient sealing, the bearing pressures on the metal surfaces should be greater than the water pressure, as is usual between a hydraulic valve and its seat.

Metal piston rings are presumably used because, irrespective of leakage, they last much longer and require less maintenance than soft automatic packing, which will give 100% water seal when new.

Did Mr. Lloyd enquire into the amount of leakage past these rings and, if not, what quantity of water might reasonably be expected to pass new metal piston rings fitted into one of the Appleby-Frodingham pistons with high-pressure water on the one side ?

In my view, a piston should never be used if two single-acting rams may be used, because the machined surfaces of cylinders are seldom as good as the external surfaces of rams; packings, particularly soft ones, cause more wear of cylinder walls than of ram surfaces.

Mr. **L. N. Lloyd**: I have made enquiries about the Lockwood and Carlisle piston rings on the melting-furnace tilting cylinders. After 25 years' use, the melting-furnace cylinders are in process of being rebored. The mixing-furnace cylinders have also been rebored recently, for the second time in 25 years. The mixer is, of course, tilted more often than the melting furnaces.

After reboring, the assembly is tested under hydraulic pressure. With pressure applied at one end only, the piston rings are found to be pressure-tight. This is confirmed by the fact that after reboring there is no tendency for the furnace to creep when in the teeming position with the operating valve closed. Before reboring, the operating valve had to be held slightly open to overcome the tendency of the furnace to return to its normal position.

## CORRESPONDENCE

Mr. **P. Linton** (The British Hydromechanics Research Association) wrote: In the first part of the paper, which deals with accelerating flow in the main during the operation of the cross-cut shears, no details of the pressure gauges used during the tests are given. If ordinary Bourdon gauges were used, with a natural frequency of about 10 cycles, the pressure drop which must have taken place within less than 0·3 sec. cannot have been faithfully recorded. This in turn throws much doubt on the remainder of the calculation based on it.

The formula for acceleration head developed in Appendix I and quoted at the beginning of the paper applies only where the velocity changes comparatively slowly or the pipeline is short. In the present case, where the flow is accelerated in about 0·3 sec., it is essential to take into account the elastic properties of both liquid and pipe by the use of the ordinary pressure-

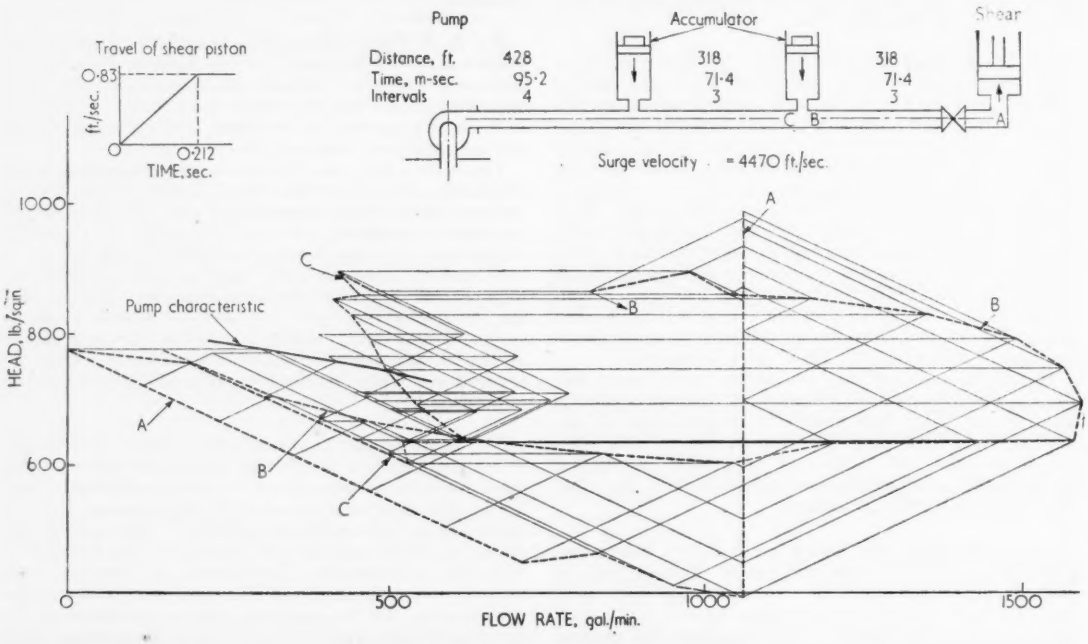



**Fig. A—Surge diagram**

surge theory. This can readily be done by a graphical method, which also gives a clear picture of the pressure and velocity changes in all parts of the system.

I have attempted to determine in this way the pressure drop corresponding to the second test (Table II of the paper). Unfortunately, a number of data were omitted from the paper, such as the distance from the pump to the first accumulator and the force/distance characteristic of the cross-cut shears. I have therefore based my calculations on the results derived by the author, *i.e.*, that the shear ram is accelerated linearly from 0–0·83 ft./sec. in 0·212 sec., and then continues at constant velocity. A comparison between the results thus obtained and the measured pressures in Table II on which the author based his calculations shows the error involved in the assumption that water is incompressible.

Figure *A* is the surge diagram up to the instant when the pressure at the ram reaches its maximum, and gives details of the layout used in its construction. Friction losses have been left out of account, since they are negligible compared with the pressure changes. The letters *A*, *B*, and *C* in the figures refer to conditions at the shear, and the downstream and upstream connections of the accumulator respectively, as shown in the diagrammatic layout. The pressures thus obtained are plotted against time in Fig. *B*(i).

The pressure at the shears falls to below 400 lb./sq. in. and rises later to almost 1000 lb./sq. in. The ' accelerating head,' or pressure difference between accumulator and shear cylinder, reaches a maximum of 207 lb./sq. in., compared with the 150 lb./sq. in. given by the measured values in Table II. This difference represents solely the error due to the incompressible water formula, since both calculations are based on the same acceleration time of 0·212 sec.

The divergence in the flow rates is even more striking. Figure *B*(ii) shows first the flow demanded by the shear cylinder and then the flow rate at the accumulator, both derived from the surge diagram of Fig. *A*. The two differ, since the water is elastic and the flow rates at the two ends of a pipe subject to pressure changes cannot be identical. The maximum flow rate at the outlet *B* of the accumulator is 1592 gal./min.; of this, 1044 gal./min. is supplied by the accumulator and the remaining 548 gal./min. comes from the pumping main. The corresponding values derived by the author are 770 and 280 gal./min. (*see* Table II). It appears therefore that the bulk acceleration formula leads to serious errors when the time during which the change takes place becomes comparable with the period $2L/a$ of the pipe section considered ($L$ = length, $a$ = surge velocity).

## AUTHOR'S WRITTEN REPLY

Mr. **L. N. Lloyd** wrote in reply: We considered that for the purpose we had in view the results would be sufficiently accurate if water were treated as incompressible, and this proved to be the case. It should be noted that the acceleration head formula on p. 272 of the paper only purports to give the terminal conditions at the end of the acceleration period; it is based on the assumption of constant acceleration, and the results should be sufficiently accurate for the low acceleration rates that prevailed.

The first accumulator to which Mr. Linton refers has no effect on the happenings in the plate mill. The 10-in. pump delivery manifold branches at the pump house into two 8-in. and one 3-in. pipes; one 8-in. pipe goes to the plate mill and the other to the melting shop. The first accumulator is in the melting-shop branch about 400 ft. from the pump manifold. Observations show that it only discharges to meet heavy requirements in the melting shop. Thus the supply to the shears under consideration was divided between the mill accumulator and the pumps. In regard to the supply and division of water between the pumps and the accumulator, it is difficult to see how these could be so large unless they were very transient. This is specially so when one considers the overall capacity of the pumps and their falling pressure/discharge characteristic.

Since the paper was written, ciné-camera observations were made of the movement of the shear rams; a pointer attached to a shear ram moved over a linear scale. The films showed the constant velocity portion of the stroke to have a displacement rate similar to that given on p. 274 of the paper, being 1000 gal./min. in one exposure and 760 gal./min. in another. During the early part of the stroke, the graphs were akin to constant acceleration, but more observations must be made to verify this.

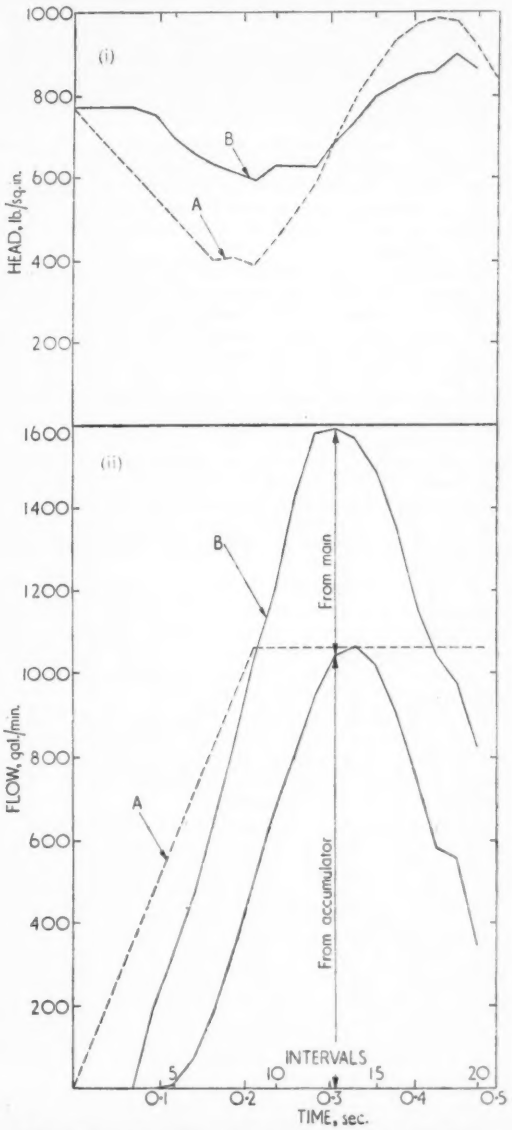



**Fig. B—(i) Pressure diagram; (ii) flow diagram**

*PROCEEDINGS OF THE AFTERNOON SESSION:* 2 P.M. to 4 P.M.

## Discussion on the Paper—

# PUMP DESIGN AND APPLICATION IN IRON AND STEEL WORKS*

Mr. **C. G. Evans** and Mr. **P. L. Fairfield** of the Harland Engineering Co., Ltd., presented their paper. In doing so, Mr. Evans made the following references to the proceedings at the morning session:

In regard to Michell bearings, a better method is for the bearing to be set to carry the load all the time. The balance disc is set 0·005 or 0·010 in. clear of its stationary face with the Michell bearing pads hard up against their thrust face. The bearing therefore carries the load while starting, running, and stopping. The balance disc can never touch its face, and so there is no dry abrasion. The balance disc then acts as a pressure-reducing component to avoid high pressure on the delivery-end gland.

Mr. Lloyd referred to the impinging of the jet after the valve or orifice. We always follow a high-pressure orifice with a velocity-reducing chamber, which allows the jet to discharge into a tube of water about 8 in. in diameter by 4 ft. 6 in.–6 ft. long, and minimizes the erosion difficulty.

The damage to the impellers that Mr. Lloyd mentioned may have been caused by cavitation, and also possibly by very low capacity flow through the pump for very long periods, when water, instead of flowing through an impeller into the guide port, tried to re-enter the impeller, and the blades of the impeller cut through the returning streams of water; there might also have been high forces on the blade tips contributing to the damage.

Such prolonged operation may lend itself to delivery-end cavitation on both impeller periphery and diffuser-blade inlet. This is especially so where the blade tips of the former have a minimum clearance from the latter, and also where the diffuser blades depart from a point pickup, *i.e.*, if they are at all flat or if the pickup angle is too low.

So far as the centrifugal pump is concerned, the accumulator is good for dealing with spray-nozzle application, because it irons out the shock to the pump from violent fluctuations in quantity, which cause axial fluctuations on the shaft. Such oscillations without a Michell bearing cause balance-disc wear.

Mr. **L. N. Lloyd** (Appleby-Frodingham Steel Co.): It is good to hear of commercial firms devoting themselves to such specialized problems as descaling. The experience gained is helpful to steelworks engineers, and Mr. Fairfield's firm is to be congratulated.

The problems in a reversing plate mill are somewhat different from those in a continuous strip mill, mainly due to the varying widths and lengths of the plate and the possibility of the plate coming out with a turned-up end. The former causes great variation in both the rate of flow and quantity required on consecutive plates. From time studies at the slab mill and the two plate mills at Appleby-Frodingham, it was found that the actual rate during a pass might be as much as six times that of the average rate on a time basis. From this it appears that an accumulator is essential for economical working with such a plant. The studies also provided information about the size of accumulator required.

The common practice of inclining the spray nozzles away from the mill stand washes scale off the plate and prevents it from being rolled in again, as might be the case if the nozzles were inclined towards the rolls. Furthermore, there is generally some end-play in the roll-neck bearings of a reversing mill, and so it is desirable to wash the scale away from the mill.

In a reversing mill, the canopy referred to in my paper is important since, owing to varying slab widths, the water from uncovered bottom nozzles needs to be kept under control. Theoretically, the kinetic energy of the jet is sufficient to carry it to the roof. The canopy is also necessary because of flying scale.

The header should be so designed that it does not interfere with roll changing, and when not in use is clear of a turned-up plate; this is necessary both to avoid damage and to prevent loss of time through such a plate jamming between the header and the roll. Plates may turn up as much as 3 ft. 6 in. high at the end, and occasionally wrap round the top roll.

Referring to an oscillating header, has Mr. Fairfield done any work on a stuffing box suitable for such an application?

In regard to valve operating times, referred to in the discussion, some ciné films have since been taken of the thrustor-operated Crowe valves referred to on page 280 of the Appleby-Frodingham paper. The camera was operated at 16 frames/sec. and the valve opening time was 0·25 sec. Obviously, a relay of the type shown in Fig. 14 should operate in much the same time, but can be slowed down by the restrictor valves shown. The relay shown in Fig. 13 was also photographed and was found to take 1·5 sec., the lift being 1 in.

Mr. **J. G. Frith** (Davy and United Engineering Co., Ltd.): The control unit for an air-hydraulic accumulator shown in Fig. 10 of Mr. Lloyd's paper has worked well, but it has one slight disadvantage in that the mechanical parts are fitted in the pressure zone. It is better to keep as much out of this pressure zone as possible; another type has been evolved which uses a float-mounted magnet actuating external switches.

On the question of direct pumps *versus* accumulators, there is no doubt that each has its own sphere, and there are applications where the accumulator cannot be dispensed with. An air-hydraulic accumulator such as that described has advantages over the ordinary weight-loaded type; it has no glands, no inertia of mass, and is not difficult to maintain.

It is generally agreed that centrifugal pumps are better for large volumes at comparatively low pressures. What are Mr. Evans's views on their use as high-pressure pumps serving presses? In two plants in the U.S.A., large presses are worked direct from three or four of these pumps in tandem, but the idling losses must be great. When should such a pump be stopped and started, and when should it be run continuously with a leak off? This depends no doubt upon the pump size and the extent to which it is stopped and started, but information upon this point would be welcome.

As regards Mr. Fairfield's paper, has consideration ever been given to making the spray-nozzle orifice disc in tungsten carbide or some other hard-wearing material to overcome the wear and erosion that he mentions?

* *J. Iron Steel Inst.*, 1952, vol. 170, pp. 360–374

Mr. **P. L. Fairfield**: Mr. Lloyd raised the question of protection against the sprays, particularly the lower ones. In Fig. *A* there is a baffle over the top, about 3 ft. above the lower jet. Mr. Lloyd exaggerated a little when he spoke of the possibility of removing the skylights, because, although there is a big pressure, the water will not spray much more than about 18 ft., by which time it will have disintegrated into a rain. On most installations, the sprays are angled towards the mill. The object is twofold: first, to use the scale-breaking effect of the mill beforehand, thereby cracking the scale and making the work of the jets easier, and secondly, to get the water deflected on to the rolls, serving the additional purpose of roll-cooling.

Figure 18 showed a header design for a continuous bar mill; it was manufactured in two halves. A shear bolt held the upper half, which could yield in the event of a cobble. The problem on the reversing mills is different, and more difficult to answer. The plate may enter a mill with the nozzles located on the ingoing side, and if a cobble occurs, the nozzles may not be touched during the forward pass, but could be wiped off by the return. This problem is ever-present, and there seem to be two answers. One is to treat the sprays as expendible, which (apart from the cost of the sprays themselves) can be difficult, and even dangerous, owing to the high-pressure flow from the breakage. The other method is to protect them with a sufficiently heavy girder of some type, which may entail difficulties on the actual mounting. We have a scheme in hand by which we have a protecting cast-steel girder in front of the sprays to withstand a cobble. It is not yet in action, so that I cannot say whether it will be successful, but it is a heavy member which should effectively protect the nozzles located beside it.

We have not had any experience with stuffing boxes for rotary or movable joints, but on some of the mills in the U.S.A. they have used, with a great deal of success, a rotary joint that is marketed over there. There is a flexible type of joint in this country, but it has yet to prove itself equal to that available in the U.S.A. I see no reason why these joints should not be used for the feed to the upper headers so that the nozzles can be swivelled well out of the way.

The problem of the 10% variation of accumulators is one that I have already discussed with Mr. Frith. The pump manufacturers are not very keen on adhering to a 10% variation. The pump can be designed to work quite effectively over as much as a 25% variation in pressure. A 10% variation on the air-hydraulic accumulator system gives ten times more air to the water; with 25%, it is only four times. Therefore, there is much less volume of air that has to be stored in heavy bottles, and the installation is cheaper. The closed valve head on the pump at no-demand can be arranged to be within the design capacity of the accumulator, and there is no need for any unloading devices. The question of the 10% variation on the accumulator has entered into many installations in this country, but there seems to be no reason why we should adhere to it. It has nothing to do with the insurance, or anything like that.

The biggest advantage of continuous pumping is its simplicity. There are no accumulators—there is, in fact, nothing but the pump and the motor and its associated valves. When maintenance, a very important matter on installations of this type, is considered, the loss of efficiency is definitely offset by reliability. I believe that the projected installation at Appleby-Frodingham for descaling was never installed because it was over-complicated. There has been a tendency to go to extreme measures to get efficiency on these installations, when a simpler scheme, perhaps sacrificing efficiency, would have given reliability.

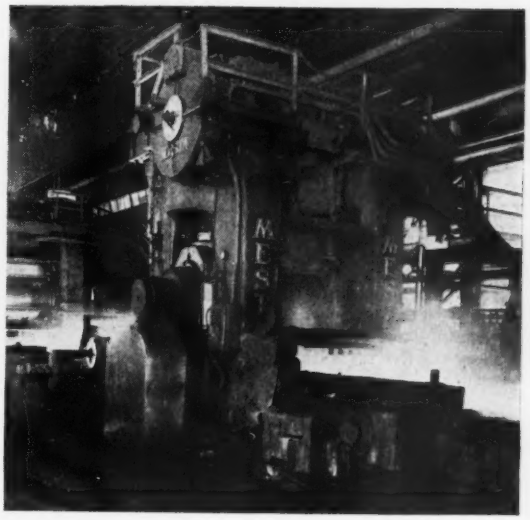


**Fig. A—Descaling nozzles mounted on a continuous strip mill. Nozzles are located both above and below the strip.**

In cross-rolling on a plate mill, the spray may theoretically only be required for one or two seconds, but I doubt whether a valve can offer such exact control. Very few valve manufacturers offer a valve that is capable of operating more often than once in 10 sec. From the pump point of view, particularly on the direct feed, it is not too satisfactory, because the pump never has time to settle down to any particular output.

In answer to Mr. Frith, a nozzle with tungsten carbide insets is being developed. It is hoped to obtain ten times more life from such a nozzle.

Mr. **G. C. Evans**: In answer to Mr. Frith, it should first be noted that there are distinct and separate fields for both the positive-action and centrifugal pumps. There is also the borderline where both can show some justification, so that each case must be settled on its merits: no hard and fast rule can be given. There have been applications of each type in the full field rightly belonging to the other, but such cases are isolated, mostly due to over-enthusiasm on behalf of either side. The result is not to the ultimate good.

Small-capacity, very high pressure duties, although capable of attainment by centrifugal units, are not ideal owing to the relatively low efficiency and the special nature of such units. It is difficult to draw a specific line, but as a guide it might be acceptable to state that (on a low-gallonage basis), while 100 gal./min. at pressures up to 1000 lb./sq. in. is a reasonable centrifugal proposition, the positive-action pump is correct for, say, 50 gal./min. or less at 1500 lb./sq. in. or more.

With reference to idling losses on a centrifugal pump, the full-speed no-demand power is between 40 and 60% of full power at the maximum efficiency point of the pump. If the rated gallonage is below the peak efficiency output, the no-flow power is obviously a greater percentage of the operating power (*see* Fig. 11).

If the duty cycle is suitable, a two-speed arrangement may be adopted, as quoted in the Supplement to the paper. In that case, the no-flow power is reduced according to the cube of the speed, so that the duty power is

first halved for no-flow and then divided by eight at half-speed, and *pro rata* for greater speed drops.

In general, where starting and stopping would be very frequent, it is preferable from pump, motor, and starter viewpoints to continue running with automatically controlled by-passes than to introduce high mechanical and electrical stresses by frequent starting. Stuffing-box behaviour is greatly improved by continuous running as opposed to starting and stopping once the packing has run in.

Supplementing Mr. Fairfield's answer to Mr. Lloyd, a wide pressure range when a hydro-pneumatic accumulator is in circuit is quite acceptable from a pump angle, and is really preferable, provided that the unit is powered initially to cover the wider power-demand range. Where no accumulator is available, a wide pressure range is bad, because of the instantaneous jumps from high flow/low pressure to low flow/high pressure.

## CORRESPONDENCE

Mr. **W. S. Allen** (Park Gate Iron and Steel Co., Ltd.) wrote: Despite the high efficiencies claimed today in certain applications of the centrifugal pump, the modern design of high-speed treble-ram reciprocating pump has been developed into a remarkably efficient unit. The no-load power consumption is much higher with the centrifugal pump than with the reciprocating type, particularly where the hydraulic power demand is intermittent. It would have been interesting if the authors could have given some information on the relative efficiencies of the two types of pump. In one works, the high-pressure hydraulic supply is provided by reciprocating pumps, with a centrifugal pump as a standby.

By giving proper attention to the water used (chemical treatment and filtering-out matter in suspension), maintenance is reduced not only in centrifugal pumps but also in pipelines, valves, etc. In the latest addition to our development schemes, my Company are paying particular attention to the treatment of water from the River Don by chemical treatment, filtration, and chlorination.

The surface quality or finish of bars is a matter of real importance today; the problem largely concerns the removal of scale during rolling. There are two types of scale, primary and secondary, the latter being the more difficult to remove. The use of high-pressure water is being rapidly developed and appears to be the solution, always provided that it is applied correctly.

Primary scale in the roughing stands can be removed by an arrangement of high-pressure water jets, together with the usual arrangement of twisting guides, which mechanically loosens and breaks up the scale. Water at low pressure used for roll-cooling is often the only medium available (if any) for removing secondary scale. But it should not be difficult to apply water at high pressures. For example, the rolling speeds in the finishing stands of a high-production mill will be 1600–2500 ft./min. A $\frac{1}{16}$-in. dia. bar will, at a speed of 1600 ft./min., have a surface area of 400 sq. ft. A high-pressure supply of 40 gal./min. through two fishtail jets divided between the last six or eight stands would mean that 1 lb. of water will impinge on 1 sq. ft. of the bar surface. This would only reduce the temperature of the bar slightly, because the contact time between the water and the bar surface is about 0·40 sec., the rise in temperature of the water being about 30° F. Could Mr. Fairfield give some information on the removal of secondary scale from small bars ?

The wrong application and misuse of high-pressure water without accomplishing the desired end can become an expensive item when you consider that a high-pressure pump of moderate capacity will require 200 kW.

On p. 373 it is stated that suitable valves for controlling sprays can only be obtained from the United States. What is unusual in the construction of these valves ?

What capacity and pressure of a boiler feed pump would the authors install for a plant with an average evaporation rate of 200,000 lb./hr. ? The boilers have to meet heavy fluctuating loads. Feed water to boilers is automatically controlled and recorded.

## AUTHORS' WRITTEN REPLIES

Mr. **P. L. Fairfield** wrote: I agree that removal of the secondary scale is the more serious problem. The primary scale is often brittle and usually cracked already, so that a high-pressure jet of water will easily remove it, especially if the bar undergoes twisting in the guides. Low-pressure sprays, such as might be used for roll cooling, are not, of course, sufficient for dealing with the secondary scale. This is usually thin, and may have been partially rolled into the bar, so that the chance of cracking assisting the sprays is slight.

Whenever water is played on hot steel, the resulting steam tends to form a barrier that prevents the subsequent sprays from effectively contacting the metal. We consider that a force of at least 6 lb./in. width of spray is necessary to penetrate this barrier and effect descaling. For high-speed mills, this figure must be at least 8 lb./in. Applying force $F = WaV^2/g$, where $W = 62{\cdot}3$ lb., $a$ = area of orifice, and $V$ = velocity of jet due to pressure, with a nozzle having a spread of 5 in. (ignoring thickness) and an efficiency of 90%, we find that an average-sized descaling nozzle requires a pressure of 960 lb./sq. in. It is therefore preferable to use the same hydraulic feed for both the primary and secondary scales.

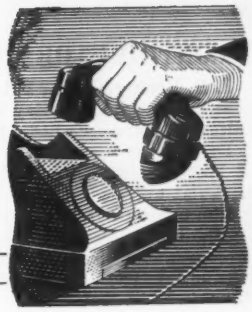
The header control valves have to withstand high pressure, and must be of large diameter and capable of frequent operation. Although similar in the former and latter respect to valves used for press control, they are often of larger capacity, and are, therefore, of special design. In the United States, the number of descaling installations has justified a commercial undertaking in considering the problem, but in the U.K. valve manufacturers have shown a reluctance to consider the requirements. Procuring the correct valve is therefore as much an economic as a design problem.

Mr. **G. C. Evans** wrote: I would refer Mr. Allen to my comments about the no-load powers in answer to Mr. Frith. As regards full pumping conditions, a reciprocating pump has admittedly a higher efficiency, but prime cost, foundations, building space, vibrational effect on other plant, etc., must all be taken into account when assessing the relative value of the two types in borderline cases. The fact that, apart from small-quantity high-pressure applications, the smaller, cheaper, smoother operating centrifugal has largely ousted the reciprocating pump speaks for itself.

I fully endorse Mr. Allen's statement about the quality of water on hydraulic and high-pressure jet systems. Maintenance time and cost, together with disturbance to production due to pump or valve outages, is decimated by care and attention to the water quality, particularly in regard to filtering out solid matter in suspension.

The question of boiler feed-pump capacity really falls into the field of responsibility of the boilermaker, together with the generation engineer, but it would appear reasonable on the facts presented by Mr. Allen to assume a pump rated capacity of about 300,000 lb./hr. Pressure is not a matter for the pump design to determine, but rather one where the pump caters for the boiler requirements. Without further information one cannot be constructive on this point, but possibly 600 lb./sq. in. boilers would be used with a pump designed pressure of about 800–850 lb./sq. in.

# N E W S



ANNOUNCEMENTS AND NEWS OF SCIENCE AND INDUSTRY

## THE IRON AND STEEL INSTITUTE

### Meeting in Swansea

The Special Meeting of the Institute to be held in Swansea from **7th to 9th October, 1952,** will open with a visit to the Trostre works of the Steel Company of Wales, Ltd., the Minister of Supply being the chief guest. In the evening of the first day the Mayor of Swansea will preside at a Reception to be held in the Brangwyn Hall.

On the second day, visits will be made to the Margam and Abbey works of the Steel Company of Wales, Ltd.; in the evening a Dinner will be held in Swansea.

The third day will be given up to visits to numerous works near Swansea. Excursions are being arranged for Ladies attending the Meeting.

### Autumn General Meeting, 1952

The **Autumn General Meeting** will be held in London on Wednesday and Thursday, **26th and 27th November, 1952.**

### Corrosion of Phosphate Coatings

A meeting organized by The Iron and Steel Institute in conjunction with the British Iron and Steel Research Association, to discuss papers on the corrosion of steel under phosphate coatings and protective finishes, will be held at the offices of The Iron and Steel Institute, 4 Grosvenor Gardens, London, S.W.1, at 2.0 P.M. on **Tuesday, 28th October, 1952.** Mr. H. T. Shirley, Chairman of the Corrosion Committee of B.I.S.R.A., will be in the Chair.

The programme is as follows:

Joint Discussion on:

"*Phosphate Coatings as a Basis for Painting Steel,*" by the Phosphate Coatings (Drafting) Panel of the British Standards Institution (Jan., 1952). (To be presented by Dr. J. C. Hudson, Chairman of the Panel)

"*Corrosion by Retained Treatment Chemicals on Phosphated Steel Surfaces,*" by S. G. Clark and E. E. Longhurst (Jan., 1952)

"*Tentative Analytical Tests for Phosphate Coatings on Steel,*" by R. St. J. Preston, R. H. Settle, and J. B. L. Worthington (Jan., 1952)

Discussion on:

"*Second Report of the Methods of Testing (Corrosion) Sub-Committee.*" (July, 1952.) (To be presented by Dr. J. C. Hudson, Chairman of the Sub-Committee.)

A few reprints of the papers are available, at 1*s.* 0*d.* each for the paper by Preston, Settle, and Worthington, and at 5*s.* 0*d.* each for the other three papers. Requests, accompanied by a remittance, should be sent to the Secretary of The Iron and Steel Institute.

The meeting will be open to all interested in the matters under discussion. There will be no charge for admission, but tickets will be required, and these are obtainable from the Secretary of The Iron and Steel Institute.

## NEWS OF MEMBERS

▶ Mr. W. D. BIGGS is on leave of absence from Murex Welding Processes Ltd., Waltham Cross, to undertake a programme of research in the Department of Metallurgy, Birmingham University.

▶ Mr. R. D. CARTER has been awarded the degree of Ph.D. of Durham University, and is now with the Plessey Co., Ltd., Ilford.

▶ Dr. EDWIN GREGORY, Director and Chief Metallurgist of Edgar Allen and Co., Ltd., Sheffield, has been elected a Vice-President of the Institution of Metallurgists.

▶ Dr. F. W. JONES, of the Brown-Firth Research Laboratories, Sheffield, has been awarded the degree of D.Sc. of Manchester University.

▶ Mr. J. T. KEMP has left the Defence Minerals Administration, United States Bureau of Mines, Washington, and has returned to the American Brass Company, Washington.

▶ Mr. H. W. KIRKBY, of the Brown-Firth Research Laboratories, Sheffield, has been appointed a Director of Firth-Derihon Stampings, Ltd.

▶ Mr. D. M. LEWIS has left the British Steel Founders' Association, Sheffield, to take up an appointment as Senior Investigator at Aluminium Laboratories Ltd., Banbury, Oxon.

▶ Mr. G. R. MORTON has left Coventry Technical College to take up the appointment of Senior Lecturer in Metallurgy at the County Technical College, Wednesbury, Staffs.

▶ Mr. J. W. POKORNY has left Messrs. Diapol, Ltd., London, to join the British Thomson-Houston Co., Ltd., Rugby.

▶ Dr. W. I. PUMPHREY, Research Manager of Murex Welding Processes Ltd., has been admitted as a Liveryman of the Worshipful Company of Blacksmiths and as a Freeman of the City of London.

▶ Dr. B. G. STREET has left the University of Liverpool to take up an appointment as Metallurgist to Brookhouse Engineering (Southport) Ltd., Lancs.

▶ Dr. C. SYKES, F.R.S., Managing Director of Thos. Firth and John Brown, Ltd., has been elected President of the Institute of Physics, as from October.

▶ Mr. G. THOMAS has been awarded the degree of B.Sc. (Hons.Met.) of the University College of South Wales, and is to carry out a programme of research at Cambridge University.

▶ Mr. G. R. WEBSTER has left England on a six-months' visit to the M.C.C. Co., Ltd., Bulawayo, S. Rhodesia.

▶ Mr. K. G. WOOD has resigned from his position as Lecturer in Metallurgy at Cumberland Technical College, to take up the appointment of Lecturer in Metallurgy at the Sheffield College of Technology.

## CONTRIBUTORS TO THE JOURNAL

**J. B. Bookey, Ph.D., D.I.C., A.R.C.S., A.R.I.C.**—Head of the Physical Chemistry Department of Scottish Agricultural Industries, Ltd., Edinburgh.

Dr. Bookey was born in London, and was educated at Haberdashers' Aske's Hampstead School and at the Imperial College of Science and Technology, where he graduated with 1st class Honours in Chemistry in 1946. As the holder of a B.I.S.R.A. bursary, he carried out a programme of Research at the College until 1948, when he joined the Physical Chemistry Department of B.I.S.R.A. at Battersea. He was awarded the degree of Ph.D. of the University of London in 1951, and spent three months in the United States, studying under the Foreign Student Summer Project at the Massachusetts Institute of Technology. Dr. Bookey took up his present appointment early this year, and is continuing to specialize in phosphorus chemistry.

**C. J. B. Fincham, B.Sc., A.R.I.C.**—Scientific Officer in the Chemistry Department of the British Iron and Steel Research Association.

Mr. Fincham was born in 1927, and was educated at the Xaverian College, Brighton, and at Brighton Technical College. In 1948 he obtained an External Degree of London University, with 2nd class Honours in Chemistry. He was elected an Associate of the Royal Institute of Chemistry in 1950. Mr. Fincham joined the staff of B.I.S.R.A. in 1948, and in 1951 was seconded to the Nuffield Research Group in Extraction Metallurgy at the Royal School of Mines, where he has been engaged in research into the fundamental chemistry of sulphur in molten silicate slags.

**K. E. Puttick, B.Sc.**—General Physics Section, British Iron and Steel Research Association. Mr. Puttick graduated in Physics at University College, London, and was later seconded to the Metallurgy Department of the Royal Aircraft Establishment, to carry out research on grain-boundary creep. He joined B.I.S.R.A. in 1950 and is at present at Bristol University, investigating the microstructure of steel with the electron microscope.

*The following are biographies of authors of papers published in the August issue of the Journal*:

**W. D. Bennett, B.Sc., Ph.D.**—Physicist at the Canadian Department of Mines and Technical Surveys, Ottawa. Dr. Bennett was born at Sheffield in 1924, and graduated from Sheffield University with the degree of B.Sc. (Hons. Phys.) in 1943. For the next four years he served as a Radar Officer in the Royal Navy's British Pacific Fleet. In 1947 he returned to Sheffield University, where for two years he studied the physical properties of superlattices, under Professor W. Sucksmith, F.R.S. From 1949 to 1951, Dr. Bennett held a Post-doctorate Fellowship at the National Research Council of Canada. He took up his present appointment in July, 1951, and is working on the development of titanium metal and alloys.

J. B. Bookey

C. J. B. Fincham

K. E. Puttick

W. D. Bennett

**Betty R. Brown, B.Sc.**—X-ray Crystallographer at British Nylon Spinners, Pontypool.

Miss Brown was educated at Twickenham County School for Girls and at Reading University, and graduated with the degree of B.Sc.(Hons.) in 1946. On leaving the University she joined the Metallurgy Division of the National Physical Laboratory as X-ray Crystallographer. She took up her present appointment in 1950.

## IRON AND STEEL ENGINEERS' GROUP

The **Nineteenth Meeting** of the Group will be held in London on **Thursday, 30th October, 1952.** Two papers will be presented for discussion: "Electric Drives for Continuous Hot Mills," by G. R. Wilson (English Electric Co., Ltd.), and "A New Continuous Hot Mill for Strips up to 24 in. Wide," by M. Langen (Loewy Engineering Co., Ltd.).

The **Twentieth Meeting** of the Group will be held in London on **Thursday, 11th December, 1952.** At the Morning Session three papers will be presented for discussion: "Experiences with the Escher Metallic Recuperator on High-Temperature Furnaces," by H. Escher (Sept. 1951, pp. 39–46); "Trials of an Experimental Austeel-Escher Metallic Recuperator," by J. B. Davis, W. Ernest, and H. Kay (Jan. 1951, pp. 66–70); and "Heat Recovery in Industrial Furnaces," by A. Clift (Nov., 1952, in the press).

At the Afternoon Session, discussion will be devoted to the paper by D. F. Marshall on "Fuel Applications in Open-Hearth Furnaces."

## BRITISH IRON AND STEEL RESEARCH ASSOCIATION

### 6th Junior Steelmaking Conference

The 6th Junior Steelmaking Conference, organized by the Steelmaking Division of B.I.S.R.A., was held at Ashorne Hill on Wednesday and Thursday, 18th and 19th June.

The first session was devoted to a discussion on the application of research results to open-hearth furnace design and steelmaking practice. Dr. A. H. Leckie, Head of the Steelmaking Division of B.I.S.R.A., outlined the work carried out on 'hot' open-hearth furnace models, and Mr. M. P. Newby, Head of the Aero-Dynamics Section of B.I.S.R.A.'s Physics Department, described work done on 'cold' models designed for the study of burner efficiency and refractory wear. Mr. M. J. McInerney, of The United Steel Companies, Ltd., Central Research and Development Department, described furnace model work (carried out in their laboratories) which had led to the development of new designs of furnaces actually built in the melting shops.

After these papers were read the meeting divided into discussion groups, which afterwards reported back in a general discussion. The general trend of the discussions was centred on how the results of research could be better applied in the works. There was a general opinion that more yet remained to be done in securing adequate collaboration between the production and research sides of the industry. Suggestions were made both for modifications in the system by which research results were reported, and for the exchange of personnel between the two sides of the industry.

In the second session, Mr. A. Jackson, Deputy General Works Manager of the Appleby-Frodingham Steel Company, read a paper on active mixer practice, in which the development of active mixer practice at Appleby-Frodingham over the last 25 years was outlined. The transfer of liquid iron from the blast-furnace to the steelworks was considered, and Mr. Jackson gave illustrations showing the considerable savings in skull losses and the improvement in refractory life when closed-type ladles were substituted for the open-top type. The development and design of the Appleby-Frodingham mixers were illustrated by means of diagrams and operational data, particularly the relation between the quantities of ore and limestone fed; the throughput of metal and the silicon and sulphur removal were given.

Mr. Jackson also discussed experiments on the ladle treatment of iron, both by additions and by the blowing of oxygen. There was a lively discussion on this subject, and it was agreed that although there were numerous tricky problems involved in the pretreatment of iron, particularly the removal of slag and dispersal of fumes, increasing metallurgical load on open-hearth furnaces made a re-examination of the economics of pretreatment a matter of vital importance.

## AFFILIATED LOCAL SOCIETIES

### Swansea and District Metallurgical Society

The list of Officers for the Session 1952–53 is as follows:

**President**

H. N. BOWEN

**Vice-Presidents**

D. L. BLEWITT — Prof. H. O'NEILL, D.Sc., M.Met.

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D. A. BISHOP — D. J. JONES, B.Sc.
J. S. CASWELL, M.Sc. — G. D. JONES
R. G. DAVIES — R. J. THOMAS
A. J. K. HONEYMAN, B.Sc. — R. WALKER

### Lincolnshire Iron and Steel Institute

The list of Officers for the Session 1952–53 is as follows:

**President**

W. L. JAMES, J.P.

**Vice-Presidents**

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W. GEARY — W. JACKSON
S. L. PUTNAM — J. A. PEACOCK
A. C. WATKISS — L. REEVE, Ph.D.

## NEWS OF SCIENCE AND INDUSTRY

### International Congress on Analytical Chemistry

An International Congress on Analytical Chemistry will be held at the Examination Schools, Oxford, under the patronage of the International Union of Pure and Applied Chemistry, from 4th to 9th September, 1952. President of the Congress is Sir Robert Robinson, O.M., D.Sc., F.R.S. The Vice-President is Sir Wallace Akers, C.B.E., F.R.I.C.

Brief details of the programme of lectures and scientific sessions were given in the News Section of the May 1952 issue of the *Journal* (pp. 99–100).

### Unified Screw Threads—Development of Services Policy and Field of Application

The Services' policy on the adoption of unified screw threads jointly agreed was last expressed in a letter of 29th September, 1950, to the British Standards Institution from the Ministry of Supply. This reviewed the vital need for a common standard and unification with the United States and the Commonwealth. It described the efforts made, in full co-operation with industry, which led up to the Declaration of Accord of 1948 with the United States and Canada, and it outlined a policy of gradual adoption of the system based on the British standard which gave effect to the Declaration of Accord.

Since that date the need for a common standard and unification has become increasingly manifest, and agreement has been reached throughout the Services and industry on British standards for bolts and nuts with unified threads (B.S. 1768 and 1769), and for screw thread gauge tolerances (B.S. 919), screwing taps (B.S. 949), and spanners for use with unified bolts and nuts (Amendment No. 1 to B.S. 192). Provision is also being made for the range to be extended below $\frac{1}{4}$-in. diameter for screws for attachment of components.

The result of this work has facilitated the production in this country of screwing tackle for the agreed ranges of sizes and pitches for nuts, bolts, and screws, and corresponding spanner sizes in the unified range, and this is now becoming available for reasonable delivery.

The Ministry of Supply, in co-operation with industry, is taking steps to ensure the widest possible adoption of the unified system for equipment and stores supplied to the Army. Similar action has been taken in the case of new aero engines coming into production, and is now contemplated for airframe and aircraft equipment production. The Admiralty has already adopted the unified system for certain types of armament and some other equipment, and, with a view to minimizing and ultimately eliminating the use of more than one system in any ship, regards the wide adoption of unified standards as a necessary development to be pursued as far and as soon as practicable.

It has all along been recognized that progress on the adoption of the unified thread for Service equipment is dependent upon mutual action with industry, and that manufacturers and their sub-contractors must, therefore, be encouraged to provide themselves with taps, dies, and other screwing tackle for the unified system.

The policy of the Service Ministries is to adopt the unified screw thread system as general practice throughout the Services, even for items of an essentially commercial nature. It is, in consequence, hoped that manufacturers will, in the light of this knowledge, be encouraged to turn over to a more general adoption of the unified screw thread system, so as to bring commercial and Services practice into line.

### Wheel Mill at Steel, Peech and Tozer

For the past two years, Steel, Peech and Tozer have been successfully operating a new type of wheel mill at their Ickles works.

Ingots are broken on a horizontal double-acting ingot-breaking machine, consisting essentially of a massive crosshead supported on anti-friction rollers and driven by a 100-h.p. 930-r.p.m. induction motor, and then passed through a continuous gas-fired counter-flow furnace. They are heated to about 1200° C. on bogies propelled by an electrically operated double-rack type push, with a thrust of 20 tons and a stroke of 9 ft. 6 in., and are then transferred to the forging press. The press is of the single-cylinder vertical four-column type, arranged for operating by two 600-h.p. hydraulic pumps and an air-loaded hydraulic accumulator with a hydraulic intensifier. The forging is formed by two operations, in the second of which the full 600-ton load of the press is used.

The forging is then transferred to a reheating furnace of the coke-oven-gas type, operating at a pressure of 5 lb./sq. in. with a calorific value of 500 B.Th.U./cu. ft. On reaching the rolling temperature it is transferred to the vertical wheel rolling mill. Its five rolls (two web, two side, and one back) roll the blank to the finished dimensions, at the same time forming the tread and rim. The blank is secured by a mandrel through the bore punched in the forging press.

After rolling, the wheel is transferred to the 1500-ton dishing press, a modified forging press driven from the pumps and air-loaded accumulator which operate the 600-ton press. Here the boss is pressed into the correct position to give the hub of the wheel its conical shape. Subsequent heat-treatment is according to the customer's specification, the majority of wheels being rim-sprayed to give a hard-wearing tread.

### Steel Tubing

Stewarts and Lloyds, Ltd., Corby, have recently completed two instructional films which show different aspects of the ' Steel Tube Age.' " Steel Pipes for Sindri " deals with the erection and laying of pipes, in sizes varying from $\frac{1}{8}$ in. to 72 in. dia., for conveying water, gas, and high- and low-pressure steam in a large fertilizer factory in Bihar State, India. This film is in colour and runs for approximately 10 min. The second film, " The Great Jib," describes the design and construction of the tubular steel jib of the W1400 walking dragline recently constructed for use in Stewarts and Lloyds' ironstone quarries, and runs for 35 min.

### Safety in the Use of Power Presses

Two important reports have recently been published by the Joint Standing Committee of the Ministry of Labour and National Service on Safety in the Use of Power Presses. The Report on the Fencing of Press Brakes (H.M.S.O., 1*s.* 3*d.*) is the third on this subject, and deals with a number of safety devices developed largely by users of press brakes. The Report on the Fencing of Hydraulic Presses (H.M.S.O., 1*s.*) proposes two forms of guard—the sliding-screen guard and the photoelectric safety device.

### Materials Handling in Industry

It is generally recognized nowadays that unnecessary handling is perhaps the greatest source of wasted time and labour in industry, and that efficient handling methods make for increased production. With the present great need for increased productivity, much thought and research are being devoted to improving handling methods. To this end, a film has been prepared by the British Electrical Development Association called " A Case for Handling," contrasting the efficiency of a factory in which materials handling has been reorganized with that of a factory where much of the work is still done by hand. Improved handling methods in a wide range of industries are depicted and explained, and their great potentialities in productivity and efficiency are emphasized.

## DIARY

**3rd–10th Sept.**—British Association for the Advancement of Science—114th Annual Meeting—Belfast.

**4th–9th Sept.**—International Union of Pure and Applied Chemistry—2nd International Congress on Analytical Chemistry—Examination Schools, Oxford.

**8th–15th Sept.**—International Geological Congress—19th Session—Algiers.

**15th–19th Sept.**—Institute of Metals—Annual Autumn Meeting—Oxford.

**16th–26th Sept.**—Cambridge Summer School in Automatic Computing—University Mathematical Laboratory, Cambridge.

**20th–23rd Sept.**—Italian Metallurgical Association—6th National Convention—Genoa.

**22nd–23rd Sept.**—The North of England Institute of Mining and Mechanical Engineers—Centenary Celebrations—Neville Hall, Newcastle-upon-Tyne, 1.

**23rd–25th Sept.**—Institution of Mining and Metallurgy—Symposium on Mineral Dressing—Royal School of Mines, Prince Consort Road, South Kensington, London, S.W.7.

**25th–27th Sept.**—Union of German Cast-Iron Technicians—Cast-Iron Symposium and 43rd General Meeting—Düsseldorf.

**27th Sept.–4th Oct.**—4th International Congress of Industrial Heat and Applied Thermodynamics—Paris.

## TRANSLATION SERVICE

(The previous announcement was made in the August, 1952, issue of the *Journal*, p. 422).

Translations Available

No. 452 (German). H. Vollmacher: " Deformation Ratios in the Thyssen Method of Rail Calibration." (*Stahl und Eisen*, 1952, vol. 72, May 22, pp. 611–616).

Translation in Course of Preparation

(German). E. Kunze: " Protective Gases for the Heat-Treatment of Steels." (*Stahl und Eisen*, 1952, vol. 72, May 8, pp. 561–569).

Charges for Copies of Translations—The charge for translations is £1 for the first copy and 10*s.* for each additional copy of the same translation. Requests should be accompanied by a remittance. These translations are not available on loan from the Joint Library.

Translations Prepared at Members' Requests—Members requiring translations of foreign papers are invited to communicate with the Secretary, who will ascertain whether they can be prepared for inclusion in the Series.

# ABSTRACTS OF CURRENT LITERATURE *and* BOOK NOTICES

## IRON AND STEEL MANUFACTURE AND RELATED SUBJECTS

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## MINERAL RESOURCES

**General Conditions of the Paleozoic Ore Deposits (Northern Spain).** P. Hernandez-Sampelayo. (*Inst. Hierro y Acero*, 1952, **5,** Jan.–Mar., 241–244). [In Spanish].

**Iron Ore Deposits of Guadramil.** J. L. Guimaraes dos Santos. (*Inst. Hierro y Acero*, 1952, **5,** Feb., *Special Issue*, 132–142). [In Spanish]. Reserves of iron ore in Guadramil in north-east Portugal are estimated at 3½ million tons.

**Geology of the Lead–Zinc–Silver–Iron Deposits of Oberzeirin in Styria.** W. Neubauer. (*Berg- Hüttenmänn Monatsh.*, 1952, **97,** Jan., 5–7; Feb., 22–27).

**Titanium at St. Keverne.** C. K. G. Laming. (*Min. J.*, 1952, **238,** Apr. 18, 395). Particulars are given of the black beach concentrates of ilmenite at Godrevy Cove, Cornwall, which might be of importance in an emergency.—T. E. D.

**Ashcroft Map-Area, British Columbia.** S. Duffell and K. C. McTaggart. (*Geological Survey of Canada*, 1951, Memoir 262). This is a report of a geological survey of southwestern British Columbia. Narrow discontinuous stringers of hematite have been found as well as some molybdite.—R. A. R.

**Geology and Coal Deposits of Minto and Chipman Map-Areas, New Brunswick.** J. E. Muller. (*Geological Survey of Canada*) 1950, Memoir 260).

**Recent Research on Saskatchewan Bentonites.** R. V. Tomkins. (*Canad. Min. Met. Bull.*, 1952, **45,** 110–112). There are, in Saskatchewan, valuable deposits of bentonite, with adequate reserves for commercial operations. Clays from the St. Victor-Pickthall area can be modified by a relatively simple process, which is considered in some detail, to produce a good drilling gel.—T. E. D.

**Mineral Resources in Nyasaland.** A. G. Thomson. (*Min. J.*, 1952, **238,** May, 472). Coal deposits of good quality have been located by the Geological Survey but there is no actual production yet.—B. G. B.

**Iron Ore in the Sahara.** (*Times Review of Industry*, 1952, **6,** May, 88). A French, Canadian, and British company has recently been formed to exploit iron-ore deposits on the western edge of the Sahara desert, in Mauritania. The provision of a port, a railway, labour, and food and water is discussed. Preliminary prospecting indicates the existence of at least 50 million tons of ore containing 65–68% of iron.

**Activity in the Mining Industry in New Caledonia in 1951.** (*Echo Mines*, 1952, Apr., 260–261). Ore analysis and production of nickel and chromium mines are quoted. Recent working of manganese ore is mentioned.—T. E. D.

**The Economic Importance of Philippine Clays and Other Local Ceramic Materials.** G. O. Opiana and I. Olayao. (*Philippine Geol.*, 1951, **6,** Dec., 5–14).

**The Federation of Malaya.** A. G. Thomson. (*Mining J.*, 1952, **238,** May, 442–443). The output of iron ore in 1951 was 846,803 tons all of which went to Japan. Coal, of a lignite type, is in great demand for home consumption only; the output in 1951 was 382,539 tons. Details of other Malayan mineral resources are given.—B. G. B.

## ORES—MINING AND TREATMENT

**The Classification of Iron Ore Reserves.** J. Hesemann. (*Stahl u. Eisen*, 1952, **72,** Mar. 13, 281–284). Of the many proposals for the improvement of the classification of iron ore reserves, the newer methods used in the U.S.A., the U.S.S.R., Germany, Britain, and Austria are cited and their usefulness discussed. The principle alterations concern the use of ' workability ' as a criterion of classification, the characterization of quantities by limits of error, and the dividing of possible reserves into ' indicated,' ' inferred,' and ' perhaps existing ' groups. It is recommended that data about iron content and accompanying elements, water content, and transport difficulties should be cited.—J. P.

**Iron Mining in Vizcaya.** R. de Gortazar. (*Met. y Elect.*, 1951, **15,** Dec., 66–70). [In Spanish]. The author traces mining developments which have led to an output of up to six million tons in the last years of the last century. Present economic conditions are sketched. Characteristics of Spanish ores are mentioned and present operations are discussed. In view of the large quantities of fines and the high sulphur content, sintering techniques will have to be considered.

**Rock Drilling with Hard Metal Bits.** T. Ekstam and E. Ryd. (*Jernkontorets Ann.*, 1952, Mar., 41–58). [In Swedish]. Drill steels with welded hard metal bits began to be used in Swedish mines in 1945–46 and by 1951 had almost completely replaced the conventional drill steel. Their use, drilling machines, methods of measuring bit wear, drilling patterns, and costs are discussed.—R. A. R.

**Quality of Sinter: Some Recent Technical Research on Improving the Product from Home Iron Ores.** D. W. Gillings. (*Iron Coal Trades Rev.*, 1952, **164,** Feb. 8. 303–309). The author outlines the results of recent pilot-plant and full-scale trials on the production of sinter from home iron ores, and discusses the effect of plant and process conditions. The assessment of sinter quality is briefly considered.—G. F.

**Lean Ores: Methods of Beneficiation in Germany.** A. E. Lance. (*Iron Steel*, 1951, **24,** Dec. 15, 565–572). The author discusses the methods of beneficiation of lean iron ores used

in Germany, dealing with pretreatment processes at the mines, wet and dry ore-dressing, sintering, magnetic separation, and pelletizing.—G. F.

**U.S.A. Exploits Low Grade Iron Ore.** R. H. Warring. (*Brit. Steelmaker*, 1952, **18,** Jan., 19–21). A description is given of the large pellet-making plant under construction at Beaver Bay, Minnesota, which will develop the vast American deposits of low-grade iron ore. It is expected that, by 1960, this and other plants will be producing 20 million tons of iron-ore pellets annually, and that within the next 25 years nearly a third of the total American steel production will come from powdered ore.—G. F.

**State Treatment Works, Irvinebank, North Queensland.** C. Elford and L. S. Jones. (*Queensland Gov. Min. J.*, 1952, **53,** Feb., 99–105). The concentration of manganese ore is described.—B. G. B.

## FUEL—PREPARATION, PROPERTIES, AND USES

**International Committee for Studies on Flame Radiation: Heat Flow Meters.** R. T. Fowler, D. A. Richardson, and M. Rivière. (*Chaleur et Ind.*, 1952, **33,** Jan., 17–20). Heat flow meters used on the experimental furnace for measuring the radiant energy received on a cold body at different parts of the furnace are described. Although the circulating-water heat flow meter is theoretically an absolute instrument, in practice, it must be calibrated, and results are given and discussed of calibrations made before and after trials.—T. E. D.

**The Causes of Fouling of the Surfaces of the Heating Chambers of Boilers, Economisers and Air Preheaters, and Means of Remedying Them.** G. Costes. (*Chaleur et Ind.*, 1952, **33,** Mar., 67–76; Apr., 107–118). There are two types of deposits, those deposited on medium- and low-temperature zones, and those deposited on high-temperature zones. The former deposits can be subdivided into powdery and caked deposits; the latter are discussed in detail. Deposits on the high-temperature zones are subdivided into fused ash, agglomerated deposits, and phosphatic deposits. The first two types are considered in detail. The prevention of deposits on heating surfaces is discussed, and means of cleaning the heating surfaces are reviewed.—T. E. D.

**Investigations into the Distribution and Valuation of Low-Grade Fuels.** H. Meyer. (*Glückauf*, 1952, **88,** Apr. 12, 335–340). New methods of sorting and correct ways of grading and analysing low-grade coals are described.—P. F.

**Example of a Coal Classification System and Its Application to Problems of Coal Preparation and Utilization.** O. Treptow. (*Glückauf*, 1952, **88,** Apr. 12, 330–331). Methods of compiling and presenting statistical data for all pits in a coal-mining area are described and their potential uses explained.—P. F.

**Characteristic Petrological Components of Coal.** C. A. Seyler. (*Fuel*, 1952, **31,** Apr., 159–170). A summary is given of the results of research on the reflectance of green light by coal and the step-like manner of its variation. Ten components derived from wood have been identified in coal and three in coke. These components change in a regular manner on metamorphism and carbonization. Detailed results of six workers are given which support the general conclusions on the discrete reflectances.—J. P. S.

**Accuracy of Sampling of Coal and Ore Deliveries.** H. Jahns. (*Glückauf*, 1952, **88,** Mar., 289–303). The Gaussian error calculus is developed with reference to sampling of coals and ores. The advantages of a reliable method of determining sampling accuracy are dealt with in sections defining the task of sampling and evaluating the economc significance of increased accuracy. The practical aspects of probability calculations are presented in detail, illustrated by examples from practice.

**Science in the Coal Industry.** Sir Charles Ellis. (*Proc. Roy. Soc.*, 1952, **212A,** Apr. 8, 1–15). Scientific and technical research in the coal industry are outlined, with special reference to coal drill design, coal preparation, coal structure, and coking.—T. E. D.

**Plant for Heavy-Media Coal Washing at the Dutch State Mines.** C. Krijgsman and P. Brichant. (*Rev. Univ. Min.*, 1952, Series 9, **8,** Mar., 65–76). Details are given of the types of liquid media available and its regeneration. A description of three different types of plant and the results obtained in them during a number of trials are given.—B. G. B.

**Methods for the Float and Sink Analysis of Coal.** (*Brit. Coke Res. Assoc.*, Technical Paper No. 3, Jan., 1952). The report details a study of the factors affecting the test, and specifies methods whereby it may be used with confidence so that the results obtained in one laboratory will be comparable with those obtained in another. The recommendations require large samples only for coal over 2 in. in size. For the desirable number of particles in size fractions, and for the combination of small size fractions, empirical rules are suggested as a basis for trial and criticism. Instructions are given for recording the results of an analysis and for drawing washability curves.—J. P. S.

**New Experiments on the Preparation of Fines with Particular Reference to Bituminous Coal Slimes.** W. Müschenborn. (*Glückauf*, 1952, **88,** Apr. 12, 340–342). The recent further development of methods used during the War, by means of which the extraction of coal slimes was facilitated by an admixture of oil is described. Kneading with oil displaces the water from the slimes, the particles becoming wetted with oil. The final separation of oily coal and water is effected with a centrifuge.—P. F.

**Coal Preparation and Its Relationship to Mineral Dressing.** E. Swartzman and L. E. Djingheuzian. (*Canad. Min. J.*, 1952, **73,** Jan., 51–57; Mar., 70–77). Stages in coal preparation are discussed, and types of crusher are surveyed. Flow sheets and sketches of various dense-media and dry coal cleaners are given. Methods of drying or dewatering coal are mentioned.—T. E. D.

**The Upgrading of Minerals, With Special Reference to Coal.** E. M. Myers. (*Chem. Indust.*, 1952, Mar. 29, 278–286). The effect of mechanization on the extraction and grading of coal is described in detail. Hand picking from a conveyor belt decreases in efficiency with fatigue of the operator, gravity separation does not necessarily remove all foreign material and froth flotation wastes the fines; the application of these methods and the new and promising technique of cyclone separation developed in Holland, similar to that used for dust collection, are treated at length. Similar methods for the enrichment of ores and minerals are described, particularly differential flotation for the simultaneous separation of more than one valuable constituent.—J. O. L.

**The Cleaning of Coal by Hand and by Mechanical Means.** W. R. Chapman. (*Trans. Inst. Min. Eng.*, 1952, **3,** Mar., 323–345).

**Production of Gas of Low Calorific Value from Wastes Obtained in Coal Preparation.** W. Puff. (*Glückauf*, 1952, **88,** Apr. 12, 343–346). Methods of exploiting the tailings from coal-washing plants and other waste matter containing coal to produce gas in an economic manner are discussed.—R. A. R.

**Coal Preparation Progress in Western Canada.** H. Wilton-Clark. (*Canad. Min. Met. Bull.*, 1952, **45,** Feb., 93–97). The relationships between size characteristics and specific gravity distribution, and difficulties encountered in coal washing are discussed. The tendency is to use air cleaning for fines, and wet washing for coarser coals. The development of cleaning techniques in western Canada from 1920 onwards is outlined.

**Postwar Developments at Maurits.** (*Coke Gas*, 1952, **14,** Feb., 43–49). The Maurits works of the Dutch State Mines is not only the largest coke-oven plant in Europe, but it is also devoted to the fullest exploitation of coal as a fuel and chemical raw material. The works layout and details of the ovens and supplementary gas producers are given. The organization of the extensive high-pressure gas grid is outlined, and gas and coke production figures are tabulated.

**From Coppee to Simon-Carves.** S. Roy. (*Tisco Rev.*, 1952, **20,** Jan., 6–8). Successive changes and developments in the coke-oven plant at the Tata Iron and Steel Co., Ltd., are described. Coppee, Drag, Koppers, Wilputte, and Simon-Carves batteries have been used and a new battery of Simon-Carves ovens is under construction.—B. G. B.

**" Lecocq " Self Sealing Coke-Oven Doors.** (*Coke Gas*, 1952, **14,** Mar., 107–108). A new design of sealing device for coke-oven doors has given satisfaction at Brussels gas works for five years. Similar installations have been fitted elsewhere by S.A. Les Fours Lecocq. The device, which is briefly described, is covered by British Patent 647,610.—T. E. D.

**The Choice of Coke-Oven Type.** S. Golczewski. (*Hutnik*, (Katowice), 1951, **18,** Dec. 481–484). [In Polish].

**Brief Reviews on Some Innovations in the Iron and Steel Industry.** D. Petit. (*Inst. Hierro y Acero*, 1952, **5,** Feb., *Special Issue*, 143–158). [In Spanish]. The author reviews the following developments: (*a*) New techniques in the construction of coke ovens; (*b*) controlled distribution in the charging of blast-furnaces; and (*c*) variable turbulence stoves as used in the trials at Denain.—R. S.

**The Economics of Coking.** R. J. Barritt. (*Coke Gas*, 1952, **14,** May, 180–182). A survey is made of the effects of costs on the economics of coke ovens. The article is based on a paper at a joint meeting of the Assoc. of Min., Electr., Mech. Eng. and the Coke Oven Managers' Assoc. in South Wales on April 10, 1952.—T. E. D.

**Calorimetric Determinations on Semi-Bituminous Coals Using Differential Thermal Analysis.** C. M. Gamel, jun. and W. J. Smothers. (*Anal. Chim. Acta*, 1952, **6,** May, 442–449). A two-hole, stainless steel sample holder was used with a 3-couple differential thermopile for the determination of thermal curves for three Arkansas semi-bituminous coals heated in air. A relation between heating value and exothermic peak area was established.—T. E. D.

**Investigations of the Swelling Behaviour of Coals and Coal Mixtures.** A. Adelsberger and H. R. Asbach. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1941, **4,** June, No. 8, 172–183). The mechanical behaviour of coals and coal mixtures on coking is examined using an automatic recording apparatus designed by H. R. Asbach for measuring expansion pressures. The ideas of mean expansion pressure and duration of expansion are introduced and, on the basis of works practice, a working scale was established to estimate the danger to a furnace of any specified coal. The connection between the temperature at the beginning of the expansion and the Ilseder number is given. It was established that, the better the quality of the coal mixture to make coke, the lower was this temperature.—R. J. W.

**An Automatic Measuring Instrument for Determining the Swelling Behaviour of Coal.** H. R. Asbach. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1941, **4,** June, No. 8, 162–171). An automatic instrument is described for the measurement of the swelling pressures in coals. It is a development of an apparatus first described by F. Korten in 1920. The coal was heated in an electric muffle furnace and the swelling pressure recorded directly on a rotating drum. The complex system of levers used and the electrical circuit diagram are clearly shown. Imperfections in previous apparatus of this kind are, it is claimed, eliminated. An additional device to measure the percentage contraction of the coal is also incorporated.—R. J. W.

**The Methods of Determining the Plasticity of Bituminous Coal.** P. Hoffmann. (*Feuerungstechnik*, 1942, **30,** Nov. 15, 249–255). Many methods of determining plasticity in coals are reviewed. An introductory discussion is given on the melting and plasticity of coals and the temperature range over which this occurs. The various methods include (*a*) direct observations, (*b*) measurement of change in length, (*c*) penetration methods, (*d*) squeezing out methods, (*e*) measurement of resistance to agitation, and (*f*) measurement of resistance to the flow of gas. The various methods are compared and the effect of experimental conditions on the numerical results shown. The importance of plasticity is discussed. (51 references).—R. J. W.

**The Methods of Determining the Baking Capacity of Coal.** P. Hoffmann. (*Feuerungstechnik*, 1942, **30,** Mar. 15, 52–57). A thorough review of the published methods for the determination of the baking capacity of coals from 1870 to 1941 is given together with important proposals for such determinations. The compression strength and the sand content of coke–sand cakes are discussed as criteria of the baking capacity. The difficulties incurred in these determinations are pointed out. In the examination of coals to be used for coking, considerations of their baking capacities are discussed.

**Concerning Methods of Determining the Swelling and Expansion Tendencies of Bituminous Coals.** W. Gröbner. (*Feuerungstechnik*, 1942, **30,** Jan. 15, 4–8). A survey is given of the methods now available for the determination of the swelling, expansion, and the contraction in coal when heated. The methods of Koppers and Jenkner, Ulrich, Bunte and Imhof, and Asbach are illustrated with diagrams. From the measurements of these properties in laboratory apparatus, it is possible to correlate them with the observed behaviour of coal in the full-scale manufacture of coke.—R. J. W.

**Some Observations on the Blending of Coals for Metallurgical Coke.** F. H. Reed, O. W. Rees, H. W. Jackman, and P. W. Henline. (Blast Furnace and Coke Assoc. of the Chicago District: *Blast Furn. Steel Plant*, 1952, **40,** Mar., 305–311, 344). The use of lower-rank coals for making metallurgical coke necessitates carefully controlled experimental work. Qualitative grouping of coals with Gieseler plastometer data is useful in selecting coals for blends in making metallurgical coke. Coal blends having Gieseler values below four or five have a strong tendency to produce cokes with a granular structure and a high percentage of breeze.—J. P. S.

**Swelling of Coals by Methanol and Its Significance.** P. Le R. Malherbe and P. C. Carman. (*Fuel*, 1952, **31,** Apr., 210–219). A study has been made of adsorption of oxygen, Freon-12, *n*-butane, methanol, and methylamine on a single coal sample up to high relative pressures. The results with $CF_2Cl_2$ and *n*-butane confirmed those for low-temperature gas adsorption, *i.e.*, they gave an internal surface of a lower order of magnitude than by heat of wetting in methanol. A modification of some of the present views on the structure of coal is necessary.—J. P. S.

## TEMPERATURE MEASUREMENT AND CONTROL

**Radiation Pyrometry: Principles of Operation, Design and Application in Steelworks.** S. S. Carlisle. (*Iron Coal Trades Rev.*, 1952, **164,** Mar. 21, 637–643; Mar. 28, 697–701). The author describes the basic principles of operation, design, and application of the various types of radiation pyrometer used in steelworks today. Their characteristics are discussed in relation to these principles with the object of assessing the suitability of a particular instrument to a particular problem. Total and partial radiation pyrometers, and optical and colour instruments, are considered separately.—G. F.

**Calibration Furnaces for Total Radiation Pyrometers.** F. Mortimer. (*Research*, 1952, **5,** Feb., 82–85). Two new furnaces designed by B.I.S.R.A. for the calibration of total radiation pyrometers are described. The laboratory furnace has a graphite tube as the heating element, and draws large currents. The portable model has a heating element formed of graphite strips pegged with alumina. This furnace requires only about 3 kW. to maintain it at 1600° C.—C. J. B. F.

**Special Purpose Applications of 'On-Off' Control (Heat-Treatment Furnaces).** E. E. Cook. (*Instrument Engineer*, 1952, **1,** Apr., 11–12). By using special combinations of 'on-off' control switches and two-point recorder-controllers, many quite elaborate automatic-control requirements can be met simply and at moderate cost. Several applications are described covering heat-treatment furnaces.—J. P. S.

**Ambient Temperature Independent Thermopiles for Radiation Pyrometry.** W. G. Fastie. (*J. Opt. Soc. Amer.*, 1951, **41,** Nov., 823–829). A major contribution to the dependence of thermopiles on ambient temperature is the temperature coefficient of thermal conductivity of the thermocouple wires. Several ambient-temperature-independent thermopiles operating at atmospheric pressure have been made either by adjusting the size of the thermocouple wires or by addition of other solid conducting supports between the receiver and the cold junctions. A mathematical analysis of the thermal system of a thermopile has led to a simplified formula for determining the proper materials and dimensions required to obtain ambient temperature independence. Any thermopile, operated at atmospheric pressure, can be made ambient-temperature-independent by the proper choice of a thermal shunt between the receiver and the cold junctions.—J. P. S.

**Use of Radiation from Incandescent Particles as an Indication of Flame Temperature.** E. K. Plyler and C. J. Humphreys. (*J. Res. Nat. Bur. Stand.*, 1951, **47,** Dec., 456–460). This is a preliminary investigation of the measurement of flame temperatures using the intensities in the ultraviolet continuum at two wavelengths, chosen in regions comparatively free from molecular bands, and comparing these energies with the continuous emission at the same wavelengths of a calibrated tungsten ribbon lamp containing a quartz window. Fuel-rich oxy-acetylene flames were used because they contain the desired incandescent particles. Flame temperatures from 1900° to 2400° C. have been determined.—J. P. S.

**Present Status of Temperature Control for Blast-Furnace Stoves.** K. Guthmann. (*Stahl u. Eisen*, 1952, **72,** Feb. 14, 185–190). The present status of temperature measurement when heating stoves is reviewed with reference to new developments, accuracy, and permissible errors. For determining true hot-blast temperatures a simple blow-off pyrometer has been developed; this works on the same principle as the suction pyrometer. For controlling hood temperatures, optical measurement with the total radiation pyrometer is better than the thermocouple. Photocell pyrometers reduce the errors which can arise through radiation from carbon dioxide and steam. The photocell can also serve to protect the hood by indicating the occurrence of flames.—J. P.

**On the Improvement of Unsteady Temperature Control by Feed-Back.** R. Klisch. (*Elektrowärme Techn.*, 1952, **3**, Apr., 25–26). Ordinary thermostatic control of electric furnaces by the 'on' and 'off' method result in 'hunting.' A new thermostat, embodying the feed-back principle, is shown and its circuit explained. By its use temperature fluctuations of the type occurring with conventional thermostats are eliminated.—P. F.

**Temperature of Moving Strip Checked Continuously at Alan Wood.** W. Walker, jun. (*Indust. Heating*, 1952, **19**, Mar., 455–460). An account is given of the complete operation of the strip mill at the Alan Wood Steel Co. In the roughing mill the temperature is recorded by a pyrometer. Heating is also checked at the reheating furnace, between the roughing and finishing mills by remote indicator and again at the finishing mill.—B. G. B.

**Temperature Measurement in Flame-Hardening.** (*Railway Gaz.*, 1952, **96**, May, 520–521). A description of the Peddinghaus Milliscope is given. A photoelectric cell is alternately illuminated with an image of the work surface and the image of a comparison filament. If the two sources are out of balance an alternating e.m.f. is produced. When in balance the e.m.f. obtained can be made to actuate relays which control the burner or quench, and, by adjusting the filament current to the correct value, an accurate control over the hardening process can be obtained. Temperatures down to 200° C. can be controlled and maintained.—B. G. B.

## REFRACTORY MATERIALS

**Differential Thermal Analysis of Clay Minerals under Controlled Thermodynamic Conditions.** R. L. Stone. (*Bull. Ohio State Univ. Eng. Exper. Sta.*, 1951, **20**, 146, 1–77).

**Heats of Formation of Quartz and Cristobalite.** G. L. Humphrey and E. G. King. (*J. Amer. Chem. Soc.*, 1952, **74**, Apr., 2041–2042). A combination of combustion and solution calorimetry was used to obtain the heats of formation of low quartz and low cristobalite from the elements. The results are $\Delta H_{298\cdot16} = -210{,}260 \pm 270$ and $\Delta H_{298\cdot16} = -209{,}330 \pm 250$ cal./mole respectively.—B. G. B.

**The Method of Determining Specific Heats of Refractory Materials at Elevated Temperatures.** (*Biuletyn Informacyjny Glownego Instytutu Metalurgii*, 1952, **3**, 2, 5–6: *Hutnik* (Katowice) 1952, **18**, Feb.). [In Polish]. A description of a calorimeter for the determination of specific heats of refractory materials at elevated temperatures and the results of some determinations are given.—V. G.

**Experimental Heat Contents of SrO, BaO, CaO, $BaCO_3$, and $SrCO_3$ at High Temperatures. Dissociation Pressure of $BaCO_3$ and $SrCO_3$.** J. J. Lander. (*J. Amer. Chem. Soc.*, 1951, **73**, Dec., 5794–5797). The high-temperature heat contents of the above oxides and carbonates have been measured using the 'drop' method in which the sample at a measured temperature in a capsule of known heat content is dropped from a furnace into a calibrated calorimeter. At 563·6° K. the observed and calculated heat contents, in calories per mole, of CaO ($H_T - H_{298\cdot16}$) were 2996 and 3009 respectively.

**Silica *versus* Basic Bricks.** T. R. Lynam. (Sheffield Metallurgical Assoc.: *Brit. Steelmaker*, 1952, **18**, Feb., 79, 81). The relative merits of silica and basic bricks for use in the basic open-hearth furnace are briefly discussed. Attention is drawn to the superiority of silcrete bricks over silica, and to the shortage of chromite which is affecting the manufacture of basic bricks.—G. F.

**A Simple Method of Determining Porosity.** K. Gustkowski. (*Hutnik*, (Katowice) 1951, **18**, Dec., 484–486). [In Polish]. An apparatus for the determination of the porosity of solids is described. Apparent volume is measured by immersion in water after previously soaking in kerosene. The volume of pores is determined with the aid of a simple mercury meter.

**Recent Research on Dinas.** R. Bárta. (*Hutnické Listy*, 1952, **6**, Sept., 417–424). [In Czech]. Developments in materials for silica bricks are surveyed, with special reference to the improvements required by roofing materials in view of modern steelmaking practice with oxygen injection. The Glass and Ceramics Department of the Prague Technical University has produced a new raw material, 'lyddite,' for high-duty silica bricks by improving the dinas. In the manufacture, high pressures were used and mechanization was improved. The chemistry of catalytic reactions and allotropic changes is dealt with and the spalling of roofs and fly ash troubles are considered. Silicon monoxide is studied; it forms from the silica at high temperatures in a reducing atmosphere.

**Critical Review of the C.T.I. Standards for Refractory Materials.** A. Palazzi and F. Savioli. (*Met. Ital.*, 1952, **44**, Mar., 103–108). The authors review the C.T.I. (Comitato Termotecnico Italiano) Standards for refractory materials, with special reference to sampling raw materials and finished bricks. The study is based on statistical methods and gives information on sampling, limits of error, and tolerances.

**History of the All-Basic Open-Hearth Furnace.** W. A. Archibald. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Pt. 1, 1–14). The progress to completely basic construction has depended on the development of special refractories and furnace structures. It has been primarily stimulated by the demand for greater uninterrupted steel output at lower cost. A review of British and foreign roof designs, refractories, and furnace performances is given together with a summary of patents relative to the all-basic furnace. (48 references).—B. G. B.

**Properties of Basic Raw Materials and Bricks.** G. R. Rigby. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part II, 15–21). The reactions undergone by the spinels and matrix minerals during the firing of chrome–magnesite bricks are briefly described. The superiority of the basic over the silica brick lies in the higher refractoriness-under-load value so that the roof can be kept hotter with an increase in output. The future development of basic bricks is discussed in relation to the use of other types of chrome ore, increase in the amount of matrix, and variation in the grading and proportion of chrome ore in the brick batch.—B. G. B.

**Performance of Refractories in All-Basic Open-Hearth Furnaces.** J. Mackenzie. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part VI, 62–68). In nearly every case the pattern of wear on the all-basic furnaces has been similar to that in silica-roofed furnaces. On the main roof, maximum wear was found over the back wall, and to a less extent over the front wall, although it was particularly bad over the charging doors. The failure of basic bricks in the main roof, walls, ramp, ends, and uptakes appears to occur in a similar manner, by a peeling mechanism. With a fired chrome–magnesite brick this is associated with the normal growth or bursting with iron oxide.—B. G. B.

**Hearth Construction and Consumption of Brazilian Magnesite in an Electric Arc Furnace.** A. A. da Silva. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, Apr., 207–213). [In Portuguese]. The method used in making the magnesite hearth is described in detail and comparative figures for refractory consumption are given for a magnesite and a zirconia hearth. Over 1200 heats were made with the zirconia hearth without any repairs.—R. S.

**Strength of Graphite Stoppers Used for Bottom Pouring.** O. Kallauner. (*Hutnické Listy*, 1951, **6**, Oct., 494–495). [In Czech]. Various methods employed in testing the strength of graphite stoppers used in the bottom-pouring of steel are discussed, and proposals for a standard test based on the author's experiments are made.—P. F.

**Basic Refractories for Cupola Service.** M. W. Demler. (*Amer. Found. Soc. Preprint*, 1952, No. 20). The author considers the reversible thermal expansion, and other properties of basic refractories, for cupola linings. Some details are given of the installation of basic bricks.—E. T. L.

**Effect of Slag on Furnace Linings.** L. B. Wyckoff. (*Amer. Found. Soc. Preprint*, 1952, No. 72). Slag erosion is a chemical effect, due to the formation of low-melting-point mixtures. The application of equilibrium diagrams to the study of this is outlined.—E. T. L.

**Attack by Acid and Basic Slags on Rammed Cupola Linings.** E. Piwowarsky and H. Schmidt. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 253–259). Experiments are described in which slag erosion of various rammed refractories was examined at 1500° and 1600° C. It was found that acid materials were attacked most vigorously by metal protoxides. As for the attack on basic materials, it was only the silica in the slag which had any effect. Recommendations on slag-resisting ramming refractories are made.—J. G. W.

**New Lithium Ceramics Have High Thermal Shock Resistance, Controlled Thermal Expansion, Chemical Resistance at High Temperatures.** R. E. Stark and B. H. Dilks. (*Mat. Methods*, 1952, **35**, Jan., 98, 99). A series of new ceramic materials, having very high thermal shock resistance, good chemical resistance at high temperatures, and a coefficient of thermal expansion which can be controlled by formulation between the limits $2 \times 10^{-6}$ in./in./° C. and $-6{\cdot}25 \times 10^{-6}$ in./in./° C.,

has recently been announced by Stupakoff Ceramic and Manufacturing Co., Latrobe, U.S.A. These ceramics are based on lithium aluminosilicate and carry the trade name Supalith. Brief details of properties and applications are given.—P. M. C.

**Long Time Load Tests on Commercial Types of Fire-Clay Brick.** J. A. Crookston and D. R. Torgeson. (Amer. Ceram. Soc.: *Indust. Heating*, 1952, **19**, Feb., 326–328). An investigation is described in which the A.S.T.M. load time procedure was modified by varying the test time and temperature and by obtaining continuous charts of the deformation. It was found necessary to hold the sample at temperatures long enough to establish a uniform rate of deformation since extrapolation, using the rate of change observed during the shorter testing times, did not give true results.—B. G. B.

**Elevated-Temperature Fatigue-Testing Machine for Ceramic Materials.** J. Dick and L. S. Williams. (*Engineering*, 1952, **173**, Apr. 4, 422–423). A description is given of a machine developed by the Engineering Laboratories of Oxford University to investigate the mechanical fatigue endurance and delayed fracture properties of simple ceramics and alumina-base 'cermets' (composite metal–ceramic bodies) at ordinary and elevated temperatures. Tests on specimens 5½ in. long have been carried out at 900° C. and, with current development, this limit will, it is hoped, be raised to 1000° C.

**Pure Oxide Laboratory Crucibles.** G. K. Stanfield. (*Chem. Age*, 1952, **66**, Apr. 26, 641–643). A survey is given of the properties and methods of manufacture of pure oxide ware as made by the Morgan Crucible Co. Ltd.—T. E. D.

**New Technique for Insulation of Expansion Joints on Gas and Air Ducts.** (*Indust. Heating*, 1952, **19**, Mar., 515–516). The technique of using mineral wool insulation is described. This type of material reduces surface cracks and hot spots and its use does not involve the need for specially constructed duct plates.—B. G. B.

## BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON

**Provision of Hot Compressed Air.** (*Oil Eng. and Gas Turb.*, 1952, **19**, Apr., 509–510). The use of gas turbines in association with a metallic blast heater to replace motor-driven or steam-turbine blowers and Cowper stoves is discussed. Flow schemes suggested include Brown Boveri's Velox blast-furnace cycle.

**The Rôle of Hydrogen in the Blast Furnace and Its Consequences.** J. G. Platon. (*Rev. Mét.*, 1952, **49**, Feb., 125–128). Trials are described which revealed a definite limit to the amount of fuel which could be injected through the tuyeres. This is ascribed to inadequate burning due to an unsuitable tuyere arrangement. The rôles of oxygen and hydrogen in the blast-furnace are contrasted.—A. G.

**Possibilities of Working the Blast Furnace " Without Air."** L. P. Dubosc. (*Inst. Hierro y Acero, Second General Meeting*, 1951). [In Spanish]. Theoretical considerations indicate that considerable advantages could be obtained by eliminating nitrogen from the cycle of reducing gases in the blast-furnace. This led to the use of a mixture of pure oxygen and the reducing gases. From a study of high-top-pressure operation, together with trials of oxygen-enriched blast, and, finally, of the sponge-iron process, practical data are built up which lead to the method of 'airless operation.' It is claimed that this process gives a reduction of 25% in coke consumption and an increase in pig-iron output of over 50%. There would be no need for powerful blowers and reheating stoves. A rich gas of high calorific value would be obtained.—R. S.

**A Comparison of Various Processes for the Production of Pig Iron, and Their Possibilities for Brazil.** H. Hellbrügge. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, Apr., 119–132). [In Portuguese]. The author reviews the manufacture of pig iron in the blast-furnace, low-shaft furnace with oxygen, electric low-shaft furnace, and the rotary Basset furnace. The heat consumption per ton of iron and the heat capacity per cubic metre of waste gas are compared in relation to the cost and availability of power.—R. S.

**Construction of an Experimental Blast-Furnace.** A. Lanari, jun. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, Apr., 176–192). [In Portuguese]. The author reviews the fuel situation in Brazil in connection with the production of pig iron by various processes and considers the methods used to improve the blast-furnace process (stock distribution, sintering, dried and oxygen-enriched blast, high top pressure). The case is made out for the installation of an experimental blast-furnace at the University of São Paulo.—R. S.

**The Humboldt Low-Shaft Furnace in Relation to the Problem of Iron and Steel Production in Portugal.** A. J. Adriano Rodrigues, R. Vargas Moniz, L. de Castro e Solla, and V. Pinto Pinheiro. (*Inst. Hierro y Acero*, 1952, **5**, Jan., *Special Issue*, 36–42). [In Spanish]. Smelting in the low-shaft furnace using Portuguese raw materials is briefly discussed.

**More Efficient Pig Iron Making.** F. Šidlík. (*Hutnik* (Prague), 1952, **2**, Apr., 81–83). [In Czech]. The use of higher blast pressures, addition of oxygen to the blast, drying the blast, and better utilization of blast-furnace gas are discussed. The operation of the Efremov expansion turbine to provide hot blast for the blast-furnace is mentioned, and a new, very efficient Czechoslovak gas-turbine plant for mixing and drying the blast is outlined.—P. F.

**Composition of Blast-Furnace Gas and Blast-Furnace Performance.** E. Schwarz-Bergkampf. (*Berg- Hüttenmänn. Monatsh.*, 1952, **97**, Jan., 1–3). The problem of determining the optimum carbon/iron ratio in the blast-furnace burden, and hence the correct coke requirement, is discussed, and nomograms are presented with which this ratio can be determined if the $CO/CO_2$ ratio of the blast-furnace gas is known. The nomogram can be used for ferric and ferrous ores, and by interpolation its use can be extended to mixed oxide ores. The extent to which the reduction proceeds directly ($4C + Fe_3O_4 = 4CO + 3Fe$) or indirectly ($4CO + Fe_3O_4 = 4CO_2 + 3Fe$) can also be determined from the graphs in a simple manner. Another nomogram giving the limiting isotherms for the formation of iron and FeO respectively in the indirect reduction of the ore, and for the formation of carbon in blast-furnace gases of different composition, as functions of the $CO/CO_2$ ratio, is also given and its use explained.—P. F.

**Reducibility of Iron Ores Used in the Blast Furnaces of the Sociedad Metalurgica Duro-Felguera.** M. Aybar Gallego and J. A. Cuesta Menendez. (*Inst. Hierro y Acero*, 1952, **5**, Jan.–Mar., 245–258). [In Spanish]. Various methods of determining reducibility are examined. The carbon monoxide method is shown to be useful for the Llumeres ore. The present hydrogen method is described and its advantages with regard to the most generally used Spanish ores are indicated.—R. S.

**Considerations on the Production of Iron.** R. Durrer. (*Inst. Hierro y Acero*, 1952, **5**, Feb., *Special Issue*, 99–104). [In Spanish]. After reviewing steel output figures throughout the world, the author considers the advantages of the low-shaft electric furnace, compared with the classic blast-furnace process. He briefly reviews the manufacture of sponge iron and the use of oxygen in iron and steel making.—R. S.

**Reducibility of Iron Ore Having a High Content of Titanium Oxide.** G. Soares de Moraes. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, Apr., 161–175). [In Portuguese]. The reducibility of ores containing 60% iron and 13·6% $TiO_2$ is studied with reference to the influence of particle size and temperature on the rate of reduction. The highest rate of reduction was obtained with about 30 mesh ore (0·5–0·6 min.).—R. S.

**Making Pig Iron Without Coke.** D. J. O. Brandt. (*Australasian Eng.*, 1952, Feb. 7, 111–123). The necessity for large-sized materials, in order that the descending stock shall remain porous in a normal high blast-furnace, is emphasized. In order to make use of more finely divided ores and fuels, low-shaft smelting is now being employed. The author briefly describes the low-shaft electric furnace, the oxygen-enriched low-shaft blast-furnace, and the briquetted charge low-shaft furnace.—P. M. C.

**Physical Conditions in the Combustion and Smelting Zones of a Blast Furnace.** J. F. Elliott, R. A. Buchanan, and J. B. Wagstaff. (*Amer. Inst Min. Met. Eng., Blast Furn. Raw Mat. Conf.*, 1952, Preprint). High-speed colour ciné-pictures at 800–3000 frames/sec. have been taken through the tuyeres of a number of blast-furnaces. The results of the study of these films are correlated with model experiments with a 1·17-in. dia. tuyere in a 4-in. thick glass-sided slice section filled with ¾-in. oak cubes, and using various air velocities. The results were treated and correlated mathematically. In other research, melting-zone conditions were simulated using glass beads and Ceresin wax with a heated air blast.—T. E. D.

## DIRECT PROCESSES

**Production of Sponge Iron in Metal Receptacles.** F. A. de Toledo Piza. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, July, 240–246). [In Portuguese]. The manufacture of sponge iron by

the Höganäs process, using metal pots instead of the usual refractory ones, is considered. Charcoal powder, which is a more active reducing agent than coke, is used.—R. S.

**Production of Sponge Iron by the Wiberg-Söderfors Process.** J. Stålhed. (*Stahl u. Eisen*, 1952, **72**, Apr. 24, 459–466). Sponge iron, prepared by the Wiberg-Söderfors process, is becoming increasingly important for the production of quality steels. A plant for this process has been in regular operation at Söderfors since 1941, with an annual output of 10,000 tons. At first charcoal was used for the manufacture of the reducing gases, but since 1950 a carburettor using coke has been in operation. Sulphur is removed from the gas by passing it through a tower of granular dolomite; 98% of the sulphur is removed. Lump ore and the usual types of sinter and pellets have been used as raw material. Pelletizing has proved particularly suitable; it is thus possible to employ a burden containing 68–70% Fe. Sponge iron is an excellent charge for the production of electric steel and it can be used, along with scrap and pig iron, in the acid open-hearth furnace. There are now Wiberg-Söderfors plants under construction in four Swedish works producing high-quality steel. The planned output is 120,000 tons/annum of sponge iron. All plants will work on magnetite concentrate in pellets.—J. P.

## PRODUCTION OF STEEL

**Iron and Steel Production.** A. Giménez y Sanmartin. (*Inst. Hierro y Acero*, 1952, **5**, Jan.–Mar., 259–281). [In Spanish]. The present state of development in the iron and steel industry is reviewed over the following fields: Blast-furnaces, converters, open-hearth furnaces, electric furnaces, refractories, rolling and forging, continuous casting, ancillary plant, inspection, testing, and research.—R. S.

**Statistical Methods in the Iron and Steel Industry.** P. Mendizabal Larumbe. (*Inst. Hierro y Acero*, 1952, **5**, Jan.–Mar., 308–313). [In Spanish]. Some production problems which were dealt with by statistical methods in the Gary Works, U.S.A., and in The United Steel Companies, Ltd., are discussed. The examples include: (1) A study of the optimum proportions of manganese and sulphur in a particular steel; (2) determining the permissible range of composition of a carbon–molybdenum steel for a given range of tensile strength; and (3) finding a good system of bar inspection.—R. S.

**Eire's Only Steelworks.** E. Plunkett. (*Brit. Steelmaker*, 1952, **18**, Jan., 14–15). The author outlines the development of the works of the Irish Steel Holdings Ltd. on Haulbowline Island in Cork Harbour. The plant, which is the only steelworks in Eire, has two open-hearth furnaces, producing 500 tons of steel per week entirely from steel scrap. A sheet mill is being installed.—G. F.

**Calcium Phosphate Melting Crucible—Metallurgy of the Basic-Bessemer Process.** G. Trömel and W. Oelsen. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 17–20: *Iron Steel Inst., 1952, Translation Series No.* 444). The FeO–$Ca_3P_2O_8$ phase diagram indicates that calcium orthophosphate should be a suitable material from which to make crucibles for investigating the equilibria between liquid iron and high-phosphorus slags. The preparation of such crucibles is described. They melt at 1820° C. and are resistant at 1600° C. to ferrous oxide and phosphate slags in the presence of molten iron. In a crucible of this type, the phosphorus content of iron was reduced to 0·025%. This implies that this degree of dephosphorization of steel should be possible in the Bessemer converter with an almost pure, solid tricalciumphosphate slag.—J. P.

**Use of Oxygen in Steelmaking.** G. Bulle. (*Inst. Hierro y Acero*, 1952, **5**, *Special Issue*, Jan., 23–35: *Iron Coal Trades Rev.*, 1952, **164**, Apr. 25, 921–929). The author describes the effects of injecting oxygen into the furnace on the steel quality and on the heating processes in open-hearth, electric furnace, and converter practices.—R. S.

**The Physical Chemistry of Desulphurization.** J. Manuel Pertierra. (*Tecn. Met.*, 1951, **7**, 325–333). [In Spanish]. The author studies the thermodynamic activity of sulphur in the metal and slag and in the furnace gases. Results show that desulphurization by basic oxides requires a high concentration of the oxide and a very slight concentration of oxygen in the bath. Strongly reducing conditions are necessary. The calculations indicate the superiority of CaO and MnO as desulphurizing agents compared with the weaker action of MgO.—R. S.

**A Survey of the Sulphur Problem through the Various Operations in the Steel Plant.** T. E. Brower and B. M. Larsen. (*Trans. Amer. Inst. Min. Met. Eng.*; *J. Met.*, 1951, **3**, Dec., 1163–1171). The authors discuss the distribution of sulphur throughout the whole series of steelmaking operations, from the coal and ore to the finished steel ingots. In particular, methods of sulphur control in the blast-furnace, external desulphurization of blast-furnace metal, the distribution of sulphur between fuel, slag, and metal, and methods of sulphur control in the open-hearth furnace, are considered.—G. F.

**Steel Desulphurization with Injected Carbide.** S. F. Carter. (*Amer. Inst. Min. Met. Eng. Elec. Furn. Steel Conf.*, 1951: *Amer. Found. Soc. Preprint*, 1952, No. 29). The method described involves injecting fine calcium carbide into the furnace bath with an inert gas. In small acid electric heats the sulphur was thus reduced from 0·085% to 0·045%.

**Possibilities of Improving Basic-Bessemer Steel by Adding Oxygen to the Blast.** W. Dick. (*Stahl u. Eisen*, 1952, **72**, Feb. 28, 233–242). Experience at the Hüttenwerk Oberhausen with a large number of basic-Bessemer heats blown with oxygen-enriched air is reported. Carbon and manganese contents in the new steels lie generally within the limits found with air-blown heats; the contents of phosphorus, oxygen, and nitrogen are much smaller. The improved quality is shown by the reduced amount of cropping and the better behaviour and freedom from cracks during rolling of ingots, as judged by data from more than 5500 heats. There are also other improvements, particularly in the drawing of wires of 5·0–5·5 mm. in dia. Railway rails of 70–85 kg./sq. mm. tensile strength made from the new steel showed a deflection, in the bend test, 2–4 mm. greater than normal Bessemer steel. On account of the importance of susceptibility to brittle fracture in killed and unkilled mild steels, a new impact test was developed using aged specimens with notches of different root radius; a statistical analysis of the results obtained showed that the improved Bessemer steel had no greater tendency to brittleness than open-hearth steel.—J. P.

**Manufacture of Basic-Bessemer Steel by Addition of Limestone Chips and Oxygen.** W. Bertram. (*Stahl u. Eisen*, 1952, **72**, Feb. 28, 243–245). Routine production, from normal pig iron containing 0·4% silicon and 2·25% phosphorus, of basic Bessemer steel with a maximum of 0·045% phosphorus and 0·004–0·007% nitrogen is carried out with certainty with oxygen-enriched blast. Limestone is added about 2 min. after the beginning of the air blow, followed by iron ore after a further 2 min. Oxygen enrichment is commenced 2 min. later; the total blowing time being 10 min. In composition and properties for many applications, the resultant steel is as good as high-grade open-hearth steel.—J. P.

**Calculating the Lime Requirements of Basic-Bessemer Heats of Different Phosphorus and Silicon Contents.** H. Kosmider. (*Stahl u. Eisen*, 1952, **72**, Feb. 28, 260–261). It is suggested that, in calculating the lime and sand additions to basic-Bessemer charges, it should be assumed that the slag will have a composition corresponding to $6CaO.P_2O_5.SiO_2$. This ensures the correct $SiO_2/P_2O_5$ ratio for good solubility of the slag in citric acid and a basicity adequate for refining, but not so high as to cause too much slagging of iron.—J. P.

**Dolomite Slinger for Open-Hearth Furnaces.** W. Gerling. (*Stahl u. Eisen*, 1952, **72**, Feb. 14, 174–176). The construction and operation of the Blaw-Knox slinger, which allows patching of the back and front walls and the hearth of an open-hearth furnace to be carried out expeditiously and without heavy manual labour, are described.—J. P.

**Why Must an Open-Hearth Furnace Have Forced Draught?** J. E. Lafon. (*Mét. Constr. Méc.*, 1951, **83**, Dec., 965–969; 1952, **84**, Jan., 47–51). The author attempts to show why forced draught for open-hearth furnaces is rational and, alone, can assure efficient preheating of the air required for good combustion. Questions of draught are considered and attention is drawn to two fundamental errors: (1) The application to gas flow of Torricelli's formula relating to water flow; and (2) the fallacious interpretation of the reading of a water column pressure drop in a Pitot tube. The work of Rummel and Leckie on air/gas ratios and flame luminosity and the development of burners and valves is discussed. A brief review is given of American methods of supplying forced draught to open-hearth furnaces and of the economics of the matter.

**Basic O.H. Steel: Calculating the Furnace Charge for Consistent Output.** J. R. Cuthbert. (*Iron Steel*, 1952, **25**, Jan., 20–24). From a study of conditions prevailing in an Indian

steelworks where output varied greatly even from heat to heat, the author puts forward a method for taking into account the varying composition of the ingoing materials. Actual charge weights and furnace performances are compared with figures obtained by the proposed method. Consistent results can only be obtained by methodical and intelligent planning.

**Present Variables Affecting Open Hearth Production in Pacific Coast Cold Metal Shops.** G. W. Teskey. (*Amer. Iron Steel Inst. Preprint*, 1951: *Blast Furn. Steel Plant*, 1952, **40,** Feb., 197–200). The author points out the effects on open-hearth production of the present quality and availability of charge materials, with particular reference to cold-metal practice in the Pacific Coast area. The main charge materials are dealt with, and it is shown how the control of the many variables has increased output in the area, in spite of the deterioration in quality of the raw materials and their short supply.—G. F.

**The Manufacture of Rimming Steel.** G. Morini. (*Met. Ital.*, 1951, **43,** Nov., 487–493). A detailed description is given of the manufacture of rimming steel in open-hearth and electric furnaces.—M. D. J. B.

**Carburizing with Oil in Open-Hearth Furnaces with Regenerative Gas and Air Preheating.** E. Fischer. (*Stahl u. Eisen*, 1952, **72,** Mar. 13, 288–290). A report is presented on the auxiliary coal-tar firing of regeneratively heated open-hearth furnaces using cold and hot metal charges. Cleaned blast-furnace gas was used as carrier gas and for atomizing the fuel, and the disadvantages of compressed air or steam atomization were thus avoided. No influence of the sulphur content of the fuel (0·84%) on the sulphur in the steel was detected; samples at melt-down showed the usual 0·04–0·05% sulphur. Obstruction and blocking of the jets did not occur during the trials, since the carrier gas flowed continuously through each burner even when fuel was fed to the other. In this way, 15–20 cu. m./hr. of blast-furnace gas were passed unburned to the checkers, but from an economic point of view, this can be neglected. The results show that a saving of coke-oven gas is possible with equal or better output, *i.e.*, under the conditions employed, about 170 litres of fuel fed to four furnaces made sufficient coke-oven gas available for a fifth furnace.—J. P.

**Theory of Heat Transfer in Open-Hearth Furnaces and Its Implications.** A. Benda. (*Hutnické Listy*, 1951, **9,** Sept., 433–439). [In Czech]. A detailed analysis is given of the relations between fuel consumption, thermal efficiency, and heat losses. Heat transfer during melting and effective regulation of gas volume are discussed. General equations for a minimum melting time and for the maximum furnace efficiency are derived, and the fuel-consumption/furnace-size ratio is determined from heat-transfer data. It is deduced that there is an optimum furnace size. The author discusses the reasons for various accepted steelmaking practices in the light of the relations deduced. Furnaces with predominantly liquid charges should be larger than those employing cold charges. Furnaces used for melting for duplexing should be small. The recent tendencies towards smaller furnaces in the U.S.A. are explained by reference to the optimum furnace.

**The Technique of Large-Scale Trials in Industry with Particular Reference to Iron and Steel Works.** J. H. Chesters. (*Iron Coal Trades Rev.*, 1952, **164,** Feb. 22, 417–422). The author reviews the techniques of planning and carrying out large-scale industrial trials and investigations, with special reference to the iron and steel industry. Among the factors discussed are the use of statistics, preliminary trials, and the evaluation and reporting of results.—G. F.

**Trials of Combustion with Oxygen in an Open-Hearth Furnace Fired with Coke-Oven Gas.** G. Husson and J. Downey. (*Rev. Mét.*, 1952, **49,** Feb., 145–162). The effect of oxygen on the chemical evolution of the process was insignificant, as was the saving on charging time. A reduction in melting time of 22·8% and in total heat time of 21·2% was observed, and production increased by 27·2% per hour of total duration. Greater economies would probably be needed to make the use of oxygen worth while, and improvements in technique are suggested.—A. G.

**The Trial All-Basic Furnaces in Great Britain and Holland.** D. C. Muir. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part III, 22–39). Full details of the design and operation of the trial furnaces are included and the main points are summarized. As no two of the trial furnaces were similar in design and operation a wide range of experience has resulted. The life of any brick, either silica or basic, is dependent to a great degree upon the design and operation of the furnace.—B. G. B.

**Stresses in All-Basic Furnace Roofs — Calculated Roof Stresses.** J. E. Pluck. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part IV, 40–46). The principles of the design of all-basic furnace roofs are derived from a study of the calculated roof stresses which depend on the shape and the chemical and physical properties of the roof brick. These principles are then discussed in relation to various present-day designs.

**Stresses in All-Basic Furnace Roofs—Calculated Roof Stresses in an All-Basic Furnace at Bilston, 1938.** J. McCracken and L. G. Stokes. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part IV, 46–50). The type of roof structure and calculated stresses for a basic roof having a successful performance in 1938 are described. With certain assumptions, a value of the stress of approximately 190 lb./sq. in. is obtained.—B. G. B.

**Stresses in All-Basic Furnace Roofs—Measurement of Interface Brick Pressures in Basic Open-Hearth Furnace Roofs.** R. M. J. Withers. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part IV, 51–56). Pairs of water-cooled plates were built into the furnace roof at selected points and liquid-filled dynamometers were placed in between; the whole unit replaced half a brick. The effect is shown of keying, spring adjustments, and warming up on the pressure between two brick faces and on the centre of pressure line between the top and bottom of a brick in a particular course. The relation between quality of bricklaying and the pressure distribution is shown. A greater roof-brick loading is obtained when the roof is restrained by a framework above than when partially suspended.—B. G. B.

**A Critical Analysis of the Results of All-Basic Open-Hearth Furnace Trials.** J. H. Chesters and J. Mackenzie. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part VII, 69–73). The all-basic furnace, because of its ability to operate at a high temperature, should be a fast furnace and must be treated as such. Operated at the rate of a comparable silica furnace it is extremely unlikely to be economic and fuel consumption will probably be higher. Several roof designs have been tried but no recommendation as to the best can yet be given. The greatest chance for improved performance still lies in the development of an improved, and if possible cheaper, basic brick.—B. G. B.

**Operating Experience on the Trial Furnaces.** J. McCracken. (*Iron Steel Inst. Spec. Rep.* 46, 1952, Part V, 57–61). The performance of the all-basic trial furnaces at Bilston, Consett, Redbourn, Templeborough and Ijmuiden is discussed from the point of view of the steelworks manager. A number of improvements are suggested.—B. G. B.

**Improved Basic Slag Control.** J. Trapl. (*Hutník*, (Prague), 1952, **2,** Feb., 37–39). [In Czech]. Improvements in the visual method of assessing slag basicity, taken from recent Soviet literature, are discussed. The use of sets of standard slag samples of known basicity is recommended.—P. F.

**Duplex Process to Obtain Steep Rise in Output.** A. Děkanovský. (*Hutník*, (Prague), 1952, **2,** Feb., 30). [In Czech]. The possibilities and advantages of introducing duplex steel production are discussed. It is stated that by using acid converters it is possible to raise the annual output of an open-hearth shop containing four 200-ton furnaces by 50%.

**High Quality Open-Hearth Steel by Duplex Methods.** A. Děkanovský. (*Hutnické Listy*, 1951, **6,** July, 330–336). [In Czech]. The author examines duplex and semi-duplex methods of steelmaking with particular reference to quality, composition, efficiency of use of open-hearth furnaces in conjunction with converters, preparation of liquid iron charge, and economic aspects. (82 references).—P. F.

**Carburetting the Open-Hearth Furnace Flame.** J. Bečvář. (*Hutník*, (Prague), 1952, **2,** Apr., 86–87). [In Czech]. The low density of coke-oven gas and some other gaseous fuels used in open-hearth furnaces leads to a low rate of heat transfer from flame to bath. The possibilities of enriching the fuel, with solid, liquid, or gaseous additions are examined. The use of about 30 lb. of tar per ton of steel was found economical and did not require special equipment.—P. F.

**Automatic Control: Installations on British Open-Hearth Furnaces.** J. D. May and W. G. Askew. (*Iron Steel*, 1952, **25,** Feb., 49–52, 59). The authors discuss the importance of automatic control of open-hearth furnaces and the advantages gained therefrom. Three typical systems on British furnaces are described in detail; they are installed on a producer-gas-fired 60-ton furnace, an oil-fired 80-ton furnace, and an oil-fired 60-ton all-basic tilting furnace, respectively.—G. F.

**Slag Pocket Cleanouts Speeded by Removable Open-Hearth Bulkhead Doors.** R. E. Over. (*J. Met.*, 1952, **4**, Jan., 26–27). The cleaning out of slag pockets on an open-hearth furnace at the Houston (Texas) plant of Sheffield Steel Co. has been speeded up by the use of top-hinged bulkhead doors, which have lasted over 1200 heats without repair. The construction of the doors and the cleaning operations are described.—G. F.

**J. & L. Dedicates 2 Million Ton Open-Hearth Shop.** (*J. Met.* 1951, **3**, Dec., 1126–1127). This article describes the new Pittsburgh works melting shop of the Jones & Laughlin Steel Corp. When complete, the shop will have eleven 250-ton furnaces incorporating many known successful design features, including suspended basic ends and port roofs. The plant will produce two million tons of steel per year.—G. F.

**Krupp-Renn Steel Plant for South Africa.** (*Engineer*, 1952, **193**, Apr. 18, 544). The Dominion Iron and Steel Corp. of South Africa is to introduce the Krupp-Renn process for the production of iron and steel from medium-grade ores. The ores, containing 44·1% to 57% Fe and an average of 24·2% $SiO_2$, are eminently suitable for the Krupp-Renn process. The capacity of the steel plant is to be 48,000 tons per annum initially, rising to 120,000 tons. Production is to commence in 1953.—M. D. J. B.

**Notes on the Manufacture of Steel by the Basic Open-Hearth Process—Special Methods.** R. Guevara Lizaur. (*Inst. Hierro y Acero*, 1952, **5**, Jan., *Special Issue*, 43–59). [In Spanish]. The author describes three methods to speed up the steel-making process: (1) At the end of the refining period the bath is covered with a reducing slag which deoxidizes the bath by diffusion; (2) the Perrin process; and (3) electric-furnace/open-hearth furnace duplexing.—R. S.

**Phase Equilibrium Investigation of the $Na_2O$–$P_2O_5$–$SiO_2$ Ternary System.** E. T. Turkdogan and W. R. Maddocks. (*J. Iron Steel Inst.*, 1952, **172**, Sept., 1–15). [This issue].

**The Free Energies of Formation of Tricalcium and Tetracalcium Phosphates.** J. B. Bookey. (*J. Iron Steel Inst.*, 1952, **172**, Sept., 61–66). [This issue].

**The Free Energy of Formation of Magnesium Phosphate.** J. B. Bookey. (*J. Iron Steel Inst.*, 1952, **172**, Sept., 66–68). [This issue].

**Thermodynamic Properties of Silicon Monoxide. An Experimental Study of the Equilibria $SiO_2 + Si \rightleftharpoons 2SiO$ and $SiO_2 + H_2 \rightleftharpoons SiO + H_2O$.** N. C. Tombs and A. J. E. Welch. (*J. Iron Steel Inst.*, 1952, **172**, Sept., 69–78). [This issue].

**The Solubility of Oxygen in Liquid Iron under Ferrous Oxide and Silica- and Lime-Saturated Ferrous Oxide Slags for Temperatures of 1530 to 1700° C.** W. A. Fischer and H. v. Ende. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 21–23). The solubility of oxygen in very low carbon iron under ferrous oxide and silica- and lime-saturated ferrous oxide slags has been determined over the temperature range 1530–1700° C. in a high-frequency induction furnace. The melts under ferrous oxide were carried out in a magnesia crucible and the others in a silica or a lime crucible. The oxygen contents under ferrous oxide and silica-saturated ferrous oxide agree with those found by Chipman and co-workers, and under the latter slags also with those found by Körber and Oelsen. The results for silica- and lime-saturated slags indicate that oxygen dissolved in the iron behaves ideally, but that the activity coefficient of ferrous oxide in the slags is less than unity. The 1400–1450° C. isotherm in the CaO–FeO–$Fe_2O_3$ system was studied by melting pure ferric oxide and lime in an iron crucible and analysing the slags. These showed that, with increasing lime, the ferric oxide content of the slag in equilibrium with iron increased, apparently due to the formation of a calcium ferrite, though it was not possible to distinguish whether this was di- or tri-calcium ferrite. Numerous petrographic and X-ray examinations showed that quenched lime-bearing slags contained metallic iron, in amounts increasing with the lime content, wüstite with up to 8% dissolved lime, dicalcium ferrite and, if the lime content were over 30%, free lime also.—J. P.

**Steel Plant Requires New River Intake.** C. W. Granacher. (*Iron Steel Eng.*, 1952, **29**, Apr., 122–126). This article describes a new river intake to provide water for the new eleven 250-ton open-hearth furnaces of the Jones and Laughlin Steel Corp. Details are given of the structural work, pumping installations, metering devices, and water-treatment plant. M. D. J. B.

**Electric Furnaces in the Iron and Steel Industry.** H. S. Newhall. (*J. Electrochem. Soc.*, 1952, **99**, Mar., 63c–64c). The development since 1918 of electric arc furnaces for the production of iron and steel is discussed.—J. P.

**Experiences with Chromite Hearths in Electric Furnaces.** A. L. Feild. (*J. Met.*, 1951, **3**, Dec., 1123–1125). The author outlines the experience of several American firms in the use of chromite hearths in electric furnaces, with particular reference to the production of stainless steel.—G. F.

**Melting Low Carbon Stainless Steel.** W. Crafts and H. P. Rassbach. (*J. Met.*, 1952, **4**, Jan., 20–25). The authors discuss the slag–metal relationships during the oxidation reduction, and addition periods in the electric-furnace melting of low-carbon stainless steel, and indicate the main trends of modern practice. Particular mention is made of a new low-carbon ferrochromium alloy, the use of which considerably reduces the alloying time and thus the danger of carbon pick-up.—G. F.

**Modern Trends in Electric Furnace and Transformer Design.** R. J. McCurdy. (*J. Met.*, 1952, **3**, Dec., 1130–1132). The author discusses recent trends in electric furnace and transformer design, which in the past decade have been towards top charging and larger furnaces, with increased transformer capacity for faster melting. With improvements in design and elimination of weaknesses which cause delays, the author believes that electric furnaces of 150 tons are practicable, and competitive with open-hearth furnaces in the field of ordinary steels.—G. F.

**A.I.S.E. Standard No. 9—Specification for Design of Hot Metal Ladles.** (*Iron Steel Eng.*, 1952, **29**, Mar., LS1–LS13). This is a tentative draft of A.I.S.E. Standard No. 9 specification and covers open-top hot metal ladles of circular or oval cross-section as used in steel mills. The specification is intended to cover only materials and the more important structural design features, such as thickness of side walls and bottom plates, and the proportions of stiffener rings.

**Carbon, Phosphorus and Sulphur Distribution in a Rimming Open-Hearth Steel Ingot Containing C 0·15%.** V. Rauner. (*Hutnické Listy*, 1952, **6**, Aug., 376–380). [In Czech]. A detailed analysis is given of the variations in chemical composition between samples taken from the melt, the finished product, and from various positions in an ingot of 0·15% carbon rimming steel cast in hot-topped, square, big-end-up moulds.—P. F.

**Volatility and Stability of Metallic Sulphides.** C. M. Hsiao and A. W. Schlechten. (*Trans. Amer. Inst. Min. Met. Eng.: J. Met.*, 1952, **4**, Jan., 65–69). The authors have determined the apparent vapour pressure of a number of metal sulphides by measuring their rate of loss of weight when heated under vacuum. They put forward a classification of sulphides which are termed ' volatile ' or ' non-volatile ' depending on whether the weight loss is mainly the result of evaporation of the sulphide molecule or of dissociation. FeS is classed as non-volatile, but about 20% of the weight loss is due to FeS transfer in the range 900–1100° C.—G. F.

**Solidification Mechanism of Steel Ingots.** H. F. Bishop, F. A. Brandt, and W. S. Pellini. (*Trans. Amer. Inst. Min. Met. Eng.: J. Met.*, 1952, **4**, Jan., 44–54). The authors describe an investigation of the solidification mechanism of experimental steel ingots, 7 in. sq. and 20 in. long, cast in hot-topped sand-bottom moulds. Temperatures in the mid-height plane were taken across both the ingot and the mould, in the former with thermocouples extending completely through ingot and mould, at varying distances from and parallel to the reference mould wall. Air-gap formation occurred after 1–1½ min. It is shown that solidification progresses in wave-like fashion at rates determined by (*a*) Carbon content, the solidification rate of lower carbon steels (0·08%) being greater in the initial stages, when the parabolic law is followed, and slower in the later stages than with 0·6% carbon steels, (*b*) superheat, which retards solidification until dissipated and thereafter has no effect; (*c*) mould wall thickness, which has a noticeable effect only in the later stages, the total solidification time being reduced by 13% in higher carbon (0·6%) steels by increasing the wall thickness from 1½ to 4½ in. The macrostructure is coarsened by increasing superheat, but is apparently not affected by mould wall thickness.—G. F.

**Cropping Losses Reduced by Electric Hot Topping.** T. L. Holmes. (*Iron Steel Eng.*, 1952, **29**, Apr., 120–122). The author describes the Kellogg electric hot-topping process, which supplies heat to the top of the metal in an ingot mould, with the metal covered by a protecting blanket of flux, to

promote solidification. The method is particularly suitable for high-grade alloy steels where a reduction in crop ends is important. Chemical analyses show that the composition of the steel is not disturbed.—M. D. J. B.

**Progress Made in the Elimination of Defects in Ingots and Rolled Rounds.** E. Blanpain. (*Tec. Met.*, 1951, **7**, Nov.–Dec., 378–383). [In Spanish]. The author reviews the defects met in ingots and rolled products, discusses faults in chiselling, and briefly describes planing, peeling, and reeling processes.

**Effect of Ingot Mold Design on Mold Life.** A. Jackson. (*Iron Steel Eng.*, 1952, **29**, Apr., 115–118). Two mould and two bottom-plate designs are compared. The two moulds are a 10-ton open top and a 10-ton taper top mould, the first with a shallow central dish and 'as-cast' surface, the second with a machined face on both the base and upper surface of the bottom-plate. The tests show an average consumption of 17·5 lb. per ingot ton on the open-top mould against only 14·6 lb. per ton on the taper-top mould. Detailed information is given on the tests.—M. D. J. B.

**Ingot and Mould: The Process of Gap Formation.** E. T. Linacre. (*Iron Steel*, 1952, **25**, Jan. 3–7, 16). The author discusses the nature of the process of air-gap formation and attempts to provide a basis for calculation of heat flow from ingot to mould. The author's calculations, together with existing evidence, suggest that, with a 3-ton ingot, gap formation starts at the bottom about 3 min. after teeming, or later with highly alloyed steel, the separation over a small area being gradual. Some of the metallurgical consequences of air-gap formation are also considered. The main conclusion is that there is insufficient evidence to decide the precise nature of the process or its practical importance.—G. F.

**Piping in Ingots and Castings.** L. Quincey. (*Mét. Constr. Méc.*, 1951, **83**, Dec., 971–977; 1952, **84**, Jan., 13–19). Piping in killed and rimming steels is discussed. Methods of conserving heat in feeder heads and the supply of heat to hot tops are mentioned. The principles and applications of electrical methods are described. A specific example is given of the electric heating of a large roll, and data are presented on levels of solidification in the roll and of volumes and dimensions of the feeder head. Electric 'hot-topping' does not cure all metallurgical ills but it can be of great assistance especially in the case of large castings when the length is many times greater than the cross-section.—R. S.

**Transverse Ingot Cracks.** N. F. Dufty. (*Blast Furn. Steel Plant*, 1952, **40**, Jan., 91–94, 130). Steps that can be taken to reduce transverse cracking are reduction in the ratio of length to cross-sectional area, corrugation of the mould walls and the use of wide-end-down moulds whenever possible. The provision of cooling racks for moulds, the maintenance of stools, hot tops, and moulds in good condition, careful pouring practice, and insistence on correct mould-dressing procedure are other salient points. The most important step in eliminating cracks is to have a properly planned casting-pit practice, and to use the right nozzle size and tapping temperature for each grade of steel. In this way two important variables, pouring rate and pouring temperature, are controlled.—J. P. S.

**Scrap Breaking.** (*Fonderie*, 1951, Nov., 2692–2695). Mechanical, thermal, and explosive methods of breaking up heavy iron and steel scrap are considered.—R. S.

## PRODUCTION OF FERRO-ALLOYS

**The Acid Smelting of Manganese-Bearing Iron Ores for the Recovery of Synthetic Manganese Ores and Their Reduction to Ferromanganese.** P. Ischebeck and J. Willems. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 1–15). The literature on the controlled oxidation and reduction of manganese-bearing iron ores to produce manganese-rich material is reviewed. Experimental melts in carbon crucibles indicated the possibility of preparing low-phosphorus manganese slags by acid smelting of such ores. Trials in a blast-furnace showed that the process could be carried out satisfactorily on a large scale, the results being in good agreement with the laboratory melts. The connection between silicon and manganese reductions, first expressed by Oelsen and Maetz in their $K_{Mn\text{-}Si}$ constant, was confirmed during acid smelting. The extent of reduction of chromium, vanadium, and manganese from the burden could be changed appreciably by varying the working temperature and the lime content of the slag. Temperature and slag basicity also control the sulphur and carbon contents of the pig iron. The production of ferromanganese from the synthetic manganese ores and the effect of temperature and basicity on the manganese oxide content of the ferromanganese slags are described. As with acid melts, there is also a connection between the silicon and manganese reductions. In conclusion, the large-scale processes used for preparing synthetic manganese ores during the late war and their respective manganese yields and coke consumptions are compared. These indicate the impossibility of producing synthetic manganese ores economically under any known conditions.—J. P.

**Electric Furnace Ferro-Alloys and Calcium Carbide.** J. H. Brennan. (*J. Electrochem. Soc.*, 1952, **99**, Mar., 61c–63c). The history of the use of the electric arc furnace in America for the production of ferro-alloys and calcium carbide, the development of the furnaces, and the preliminary treatment of the ores for producing alloys of greater purity are reviewed.

**Utilization of Mineral Resources.** D. N. Wadia. (*Metal Market Rev.*, 1952, **5**, Feb., 15–21). Owing to the extensive deposits of easily worked iron ores, often in close proximity to coalfields, India could become the chief metallurgical centre of Asia and also export either finished steels or processed iron to other parts of the world. The manufacture of a wide range of ferro-alloys could be increased to several times its present output. The export of home-produced ferromanganese in place of manganese ore should be developed.—B. G. B.

## FOUNDRY PRACTICE

**Organization of Melting in an Iron Foundry.** L. Bigard. (*Fonderie*, 1952, Dec., 2729–2737). The handling of raw materials and equipment in the stockyard, in charging, in preparation of the charge, and the devices and systems used in small and large foundries are discussed and illustrated.

**Process Planning in the Steel Foundry.** S. L. Finch. (*Foundry Trade J.*, 1952, **92**, May 29, 561–570). The author outlines means of achieving high quality and productivity. The main point is that the aim is to cast so as to necessitate little fettling; this is achieved by proper planning by a special department of the foundry, the cost of which, in the author's experience, is well repaid.—E. T. L.

**Foundry Management Looks at Statistical Quality Control.** E. L. Fay. (*Amer. Found. Soc. Preprint*, 1952, No. 34). The author points out the value of control in improving quality, and reducing scrap and salvage costs, as well as some indirect savings. He outlines the setting up of a quality control programme.—E. T. L.

**Quality Control in a Malleable Iron Foundry.** E. F. Price and O. K. Hunsaker. (*Amer. Found. Soc. Preprint*, 1952, No. 32). The author gives examples of the practical application of statistics to foundry work. He points out the need for proper data, dissemination of the information, and prompt action.—E. T. L.

**Refractory Practice as Applied to Malleable Duplexing.** C. W. Meyer. (*Amer. Found. Soc. Preprint*, 1952, No. 24). The improvement that has been made in refractory practice by experimenting with types of tuyeres and melting zone linings of cupolas, is discussed. The forehearth, transfer ladle, and electric furnace are described with respect to their design and life, as determined by the refractories used.—E. T. L.

**How Iron and Steel Melt in a Cupola.** H. W. Lownie, jun. D. E. Krauser, and C. T. Greenidge. (*Amer. Found. Soc. Preprint*, 1952, No. 43). A small cupola in operation was quenched with water, and the charge examined. It was thus possible to deduce the temperature distribution in the cupola. During the melting of pig iron, cast iron, and steel, all three components tend to oxidize on the surface until melting begins. Cast iron and pig iron melted so as to leave a shell high in sulphur but low in carbon.—E. T. L.

**Melting Tests in a Cupola with Acid and with Basic Linings under Comparable Conditions.** E. Piwowarsky and H. Schmidt. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 261–271). Experiments were performed in a conventional cupola first with an acid, then with a basic lining. In the basic cupola it is possible to remove the bulk of the phosphorus, and to desulphurize further than can be done in the acid cupola.—J. G. W.

**Physicochemical Considerations for the Operation of Acid and Basic Cupolas.** H. Schmidt. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 273–279). The author considers the physical chemistry of the cupola process and deduces the conditions which promote dephosphorization and desulphurization.—R. A. R.

**Full-Scale Tests of the Coating of Coke.** E. Piwowarsky and H. Eyckeler. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8,

Mar., 1952, 281–286). The protection of coke against reaction with $CO_2$ by coating with Portland cement (*see* 'Prerequisites for the Production of Hot Cupola Iron and the Advantages of an Effective Coke Coating,' *J. Iron Steel Inst.*, 1951, Sept., 58) leads to important coking economies, in that small coke performs as well as high-quality furnace coke. This conclusion is based on works trials performed by the authors in a 900-mm. dia. cupola.—J. G. W.

**The Importance of a Good Coke Coating for the Success of the Method.** E. Piwowarsky and G. Poel. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 287–288). The authors conclude from tests on a small cupola at the Aachen Institute, that to ensure success with the cement-coated coke, recommended by Piwowarsky and Eyckeler, the coating must be continuous and its thickness appreciable.—J. G. W.

**The Influence of the Effective Stack Height on the Working of a Cupola.** K. Krämer. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 289–292). It was found in a cold-blast cupola that lowering the effective stack height to as little as 3·5 diameters does not reduce the temperature of the iron at the spout below 1500° C. The lower stack makes the use of substantial proportions of small hard coke practicable and also reduces the sulphur content of the iron.

**Effect of the Quantity of Blast on the Superheat Temperature in Cupola Melting.** W. v. Preen. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 293–295). The author deals with the hitherto unexplained fact that the temperature of superheated iron rises with increasing blast even though the heat consumption in the melting and superheated zones increases, too. He shows that the combustion ratio must change with blast quantity on account of its dependence on the temperature gradient in the reduction zone. Small changes in this ratio will account for the above phenomenon, but owing to the inaccuracy of gas analyses this has not been confirmed in works tests.—J. G. W.

**Recent Development of Cupola Design with Special Reference to Hot-Blast.** F. Schulte. (*Foundry Trade J.*, 1952, **92,** Apr. 17, 405–414; Apr. 24, 443–447). After surveying the performance of 500 German cupolas, the author emphasizes the need for constant airflow in the shaft, obtainable only by decreasing the lining wear and using watercooling. The effect of blast preheating on the theoretical combustion temperature and coke consumption is shown in a diagram. He suggests that the shaft might be shortened by a third if hot-blast were used. Oxygen addition would not bring about much saving of coke.—E. T. L.

**Swarf Injector for Cupolas.** A. R. Parkes. (*Foundry Trade J.*, 1952, **92,** Apr. 10, 389–392). This is a description of a method of adding cast-iron swarf to a cupola (*see J. Iron Steel Inst.*, 1952, **171,** Aug., 427).

**Technical Developments in the Production of Foundry Iron.** J. Miles and F. Evans. (*Instituto del Hierro y del Acero, Second General Meeting*, 1951). [In Spanish]. Recent developments in cupola operations have made possible the production of better-quality cast iron in spite of low-grade raw materials. Duplexing, in which the cupola is combined with other furnaces, is very promising under certain economic conditions. The authors discuss: Systems of charging; slag removal; stabilized dolomite linings; and the cupola/electric-furnace process for the production of black-heart malleable cast iron.—R. S.

**Metallurgical Blast Cupola.** R. Doat and M. A. DeBock. (*Amer. Found. Soc. Preprint*, 1952, No. 76). A slagging cupola, developed by Compagnie Générale des Conduites d'Eau, Liége, in which charges of 90–100% steel scrap are employed, is described, and its operation and the results obtained discussed. It is provided with a blast preheater utilizing the waste gas. A heat balance, showing a thermal efficiency of 51·5%, is presented. Melting is continuous or intermittent according to requirements. The temperature of the iron is very high (2800° F.); it is completely deoxidized and of outstanding quality. The cupola can use coke of low quality, high in sulphur and ash. The slag, granulated by the cooling water from the cupola, is turned into a saleable product low in FeO which can be used for cement making.—R. A. R.

**Melting Iron in a Basic-Lined Water-Cooled Cupola.** W. Levi. (*Amer. Found. Soc. Preprint*, 1952, No. 48). This type of cupola has been used to give low-sulphur high-carbon steels suitable for making ductile iron, or for casting. A tubular water-cooling system replaces most of the refractories in the melting zone, thus reducing erosion, and allowing continuous operation for long periods. Hot blast is applied, and a procedure has been devised for banking up the cupola between periods of use.—E. T. L.

**Improvements in Cupolas.** G. Joly. (*Fonderie*, 1952, Feb., 2805–2809). Problems of balanced blast, the hot-blast cupola, and oxygen enrichment are surveyed.—R. S.

**A Study of the Formation of Nodular Graphite.** F. Hurum. (*Amer. Found. Soc. Preprint*, 1952, No. 75). By microscopical studies the authors establish the presence of silicon carbide in nodular iron. It is then deduced that magnesium added to make nodular iron stabilizes the carbides so that a hypereutectic melt is created locally. The inoculation with ferrosilicon is thought to create the 'X' constituent (the source of the nodule nuclei), and to cause fractional diffusion in which the double precipitation of silico-ferrite and austenite alters the distribution of silicon, carbon, and iron.—E. T. L.

**On the Mechanism of Graphitization in Nodular Cast Iron.** J. M. Navarro Alvargonzalez. (*Inst. Hierro y Acero*, 1952, **5,** Feb., *Special Issue*, 174–179). [In Spanish]. Current theories explaining nodular graphitization are examined. Nodules probably do not grow radially from the centre but are formed by an interphase phenomenon which may be stimulated by surface stresses.—R. S.

**The Influence of the Quantity of Inoculation Silicon on the Mechanical Properties of Chill Castings with a Spherolitic Core Structure.** E. Piwowarsky and E. v. Gumpert. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 345–347). Experiments are described from which it appears that the depth of the hard skin on a chill casting decreases with increasing inoculation silicon, and increases after treating with magnesium. Maximum tensile and bending strengths are obtained with 0·8% silicon.—J. G. W.

**Practical Contributions on the Subject of Spheroidal Cast Iron.** E. Piwowarsky. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 311–322). This is a summary of a number of current research projects at the Giesserei Institut, Aachen, concerned with the effects of superheating basic slag treatment, basic lining, and with the best methods of introducing magnesium into the cast iron melts, including the converter method.—J. G. W.

**Quality Cast Irons by Inoculation.** V. Kleiner and J. Plachý. (*Hutník* (Prague), 1952, **2,** Mar., 61–66). [In Czech]. A survey of the most important aspects of making and using nodular cast irons is given with particular reference to the statistical work by J. Plachý and J. Čeledy on the relation of the carbon/silicon ratio to strength.—P. F.

**On the Structure of Spheroidal Cast Iron.** A. Wittmoser. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 323–333). Following earlier work on some fundamental differences between ordinary and spheroidal iron in their primary structures, the author reports the presence of different types of inclusions in spheroidal iron, and up to seven compounds in magnesium-treated iron, of which magnesium nitride, sulphide, and phosphate were found by chemical analysis. The author regards these findings as confirmation of his earlier view that magnesium does not purify the iron. On the contrary, this treatment increases both the variety and the number of inclusions. (52 references).

**Effects of Cerium on Graphite Formation in Alloy Cast Iron.** E. A. Rowe and H. A. Johnson. (*Amer. Found. Soc. Preprint*, 1952, No. 1). This paper concerns the effect of cerium on cast iron alloyed with nickel, manganese, and molybdenum. It tends to lower the tensile strength, though this can be prevented by adding a secondary inoculant. The type and amount of secondary inoculant affect the amount of acicular pearlite produced. The most desirable physical properties were obtained with 0·04–0·05% cerium added with 1·0–1·2% silicon in the form of ferrosilicon.—E. T. L.

**Spheroidal Graphite Iron up to Date.** W. W. Braidwood. (Inst. Brit. Foundrymen: *Foundry Trade J.*, 1952, **92,** Mar. 27, 323–329). The author considers the terms 'spheroidal' and 'nodular.' Various castings of spheroidal graphite iron are illustrated and their properties discussed.—E. T. L.

**Effect of Phosphorus Content on Graphitization Rate and Mechanical Properties of Black-Heart Malleable Iron.** J. E. Rehder. (*Amer. Found. Soc. Preprint*, 1952, No. 8). Phosphorus leads to a decrease of elongation, but increases the ultimate strength, yield strength, and hardness. The ratio of yield to ultimate strength increases with increasing phosphorus. The main disadvantage is that, in malleable iron, phosphorus retards annealing.—E. T. L.

**Solidification of Nodular Iron in Sand Molds.** R. P. Dunphy and W. S. Pellini. (*Amer. Found. Soc. Preprint*, 1952, No. 9). Determination of the thermal gradients in a cooling block of nodular cast iron shows that solidification is slower than in grey iron.—E. T. L.

**Air Furnace Refractory Practice in Cupola-Air Furnace Duplexing.** W. C. Corbeau. (*Amer. Found. Soc. Preprint*, 1952, No. 27). The air furnaces used in conjunction with two cupolas for preparing malleable iron at the works of the National Malleable and Steel Castings Co., Cleveland, Ohio, are described with special reference to laying the refractories.

**Use of Triplex Process in Steel Foundries.** (*Fonderie*, 1951, Dec., 2742–2746). The Triplex process consists of melting the scrap in a 3-ft. dia. cupola, decarburizing the liquid iron in a 2-ton acid converter and refining the steel in a 2-ton electric arc furnace. The author calculates the cost of making a ton of liquid steel from scrap in the cupola-converter process and in the arc furnace. The cost of refining the liquid metal in the arc furnace, either from the converter or steel made in the arc furnace, is given separately. The Triplex process does not result in a decrease in production costs; its sole advantage is in increased output of a high-quality metal.—R. S.

**Effect of Heating Rate on Malleablizing and the Formation of Temper Carbon.** J. H. Ubbink. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 335–337). The author reports that the number of temper graphite nodules in black-heart malleable iron made by the cupola/electric-furnace process increases with the time taken to traverse the 250–350° C. range, during heating up. This relationship is unaffected by cooling after traversing this temperature range and preceding the annealing treatment proper.—J. G. W.

**New Technological Processes in the Production of Malleable Cast Irons in the U.S.S.R.** Z. Hostinský. (*Hutnické Listy*, 1951, **6**, July, 323–330). [In Czech]. The practical implication of recent research into the properties of cast irons, primarily those of the inoculated type, is discussed with special reference to the work of A. P. Toropanov. Heat-treatment, superheating the melt, optimum manganese/sulphur ratios, graphitization, and other aspects are considered, and developments and possible improvements indicated. Comparisons of production methods and qualities of inoculated cast irons in Europe, the U.S.S.R., and the U.S.A. are made, and the nature and origin of differences discussed.—P. F.

**Effects of Melting Furnace Atmosphere on the Fluidity, Hot Tearing Tendency, and other Properties of Malleable Iron.** E. A. Lange and R. W. Heine. (*Amer. Found. Soc. Preprint*, 1952, No. 13). Metal held for 1 hr. at 2700° F. lost no silicon or manganese, whatever the atmosphere, although carbon is rapidly oxidized out by $CO_2$, $H_2O$, or air, and removed slowly by hydrogen. Atmospheres of $CO_2$, $H_2O$, nitrogen, hydrogen, or argon all cause a decrease in fluidity. Increased carbon content increases the tendency to hot tear, but a hydrogen atmosphere improves the resistance to hot tearing.—E. T. L.

**Modern Malleablizing Furnaces for Annealing in a Gas Atmosphere.** F. Schulte. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 339–344). The author describes various furnaces suitable for annealing malleable iron in a gas atmosphere, as used in the United States and England.

**Malleable Iron Annealing Time Reduced.** W. G. Wilson and N. F. Tisdale, jun. (*Amer. Found. Soc. Preprint*, 1952, No. 41). The addition of about 0·0015% boron to malleable iron makes it possible to reduce the annealing cycle. In the first stage of annealing at 1600° F., the cementite in the iron with the boron decomposed entirely within 8 instead of 16 hr. In the second stage of annealing at 1350° F., the boron addition causes almost complete decomposition in 8 instead of more than 24 hr.—E. T. L.

**50 Years' Co-operation Pays Dividends in Steelfounding.** F. Rowe. (*Foundry Trade J.*, 1952, **92**, Mar. 15, 81–86). The author deals with arc melting, the decline of the Tropenas converter, the power input/capacity ratio of electric furnaces, moulding sands, moulding, productivity, the British Steel Founders' Association, and working conditions.—E. T. L.

**The Use of X-Rays in the Foundry.** R. Kloda and J. Zábrš. (*Hutnické Listy*, 1951, **6**, Sept., 429–432). [In Czech]. The quality of steel castings is influenced by the accumulation of metal at junctions, particularly at those of the **T**-type. X-ray inspection of trial castings for mass production is therefore recommended. Several X-ray pictures showing faults at **T**-joints are shown and discussed.—P. F.

**Tumbling of Small and Medium Sized Castings.** (*Fonderie*, 1951, Dec., 2738–2741). This is a brief note on the construction of cylindrical and polygonal drums. Methods of charging and discharging are stated. Factors affecting the speed of rotation are given.—R. S.

**Ingot-Mould Manufacture at Richard Thomas and Baldwins, Limited, Landore, Swansea: Sandslinging Method of Mould Production.** L. H. Williams. (*Iron Coal Trades Rev.*, 1952, **164**, Mar. 14, 579–586). A description is given of the layout and method of ingot-mould production at the modern Landore works of Richard Thomas and Baldwins Ltd. Particular attention is given to the technique, believed to be unique, of ramming the sand moulds by means of sandslingers.—G. F.

**Additions to Sand before Discontinuous Milling.** (*Fonderie*, 1952, Jan., 2779–2783). Methods and equipment used for proportioning sand volumetrically and by weight before milling are described and illustrated.—R. S.

**Reclaiming Used Molding Sand by Air Scrubbing.** H. H. Fairfield, J. McConachie, and H. F. Graham. (*Amer. Found. Soc. Preprint*, 1952, No. 47). A device for reclamation in a steel foundry is described, in which dry sand is blown through a turbulent air stream, thus blowing away the fines and leaving a sand which is fairly uniform. Reclamation of the sand for use as a core sand involves twice to three times the work of reclamation for moulding. The low initial cost makes this device suitable for the small foundry.—E. T. L.

**Pneumatic Reclamation for Foundry Sands.** C. E. Wenninger. (*Amer. Found. Soc. Preprint*, 1952, No. 15). The author describes the development of a design incorporating an air scrubber, and mentions the layout and costs of a full-scale plant which has been in operation for some time.—E. T. L.

**Modernization and Mechanization of Foundries—Mechanical Preparation of Sands.** D. Iturrioz. (*Met. Elect.*, 1952, **16**, Apr., 37–40). [In Spanish]. The sand mixing mill made by the Swiss firm of Georg Fischer of Schaffhausen is described.

**Preparation of Sand Mixtures for Moulding.** J. Vazquez White. (*Inst. Hierro y Acero*, 1952, **5**, Jan., *Special Issue*, 60–72). [In Spanish]. The author describes methods of selecting moulding sands for casting various metals and for castings of various size and thickness.—R. S.

**Grain Size Measurement and Permeability of Foundry Sands.** P. Jasson. (*Fonderie*, 1952, Feb., 2795–2804). The relationship between the permeability $P$ of sands and their grain size is obtained by the equation $P = \text{constant}/F^2$ where $F$ is the grain size. Density after ramming must, however, be taken into consideration. Variations in density have sometimes explained the differences between actual and theoretical permeability. Calculations of the theoretical specific surface based on the American Foundrymen's Assoc. fineness index are discussed.—R. S.

**Mineral Perlite and Its Use in the Foundry.** E. D. Boyle and H. R. Wolfer. (*Amer. Found. Soc. Preprint*, 1952, No. 21). ' Perlite ' consists mainly of silicates in a fused glass-like form, with no free silica. The authors describe its uses in the foundry for insulation, for mixing in sands, and as a powder for ladle covering.—E. T. L.

**Olivine Application in the Foundry.** G. S. Schaller. (*Amer. Found. Soc. Preprint*, 1952, No. 80). Experiments are touched on, carried out to test the suitability of olivine as a foundry sand. It is concluded that though there is as yet no commercial producer of this mineral, it would be useful for grey iron and non-ferrous founding.—E. T. L.

**Influence of Specimen Tube Loading and Riddle Size on Molding Sand Test Results.** D. I. Huizenga and K. E. Spray. (*Amer. Found. Soc. Preprint*, 1952, No. 26). As the result of tests, the authors recommend that sand-testing equipment should be checked for wear, and that an identical procedure should be adopted in all cases.—E. T. L.

**Synthetic Resins in the John Harper Foundry.** J. W. Dews and P. H. Drury. (*Foundry Trade J.*, 1952, **92**, May 22, 535–539, 550). This company has achieved great success with urea-formaldehyde liquid resin as a core binder. The advantages are: (1) Lower cost than linseed oil; (2) lower curing and baking temperatures; and (3) much shorter drying times are required, so that high-frequency electricity can be used.

**Pattern Making to Compensate for Shrink Allowance.** M. K. Young. (*Amer. Found. Soc. Preprint*, 1952, No. 36). The use of medium- and high-expansion gypsum cements for making expanded patterns, models, and moulds is described.

**Patterns for High-Production Malleable and Steel Foundries.** J. M. Kreiner. (*Amer. Found. Soc. Preprint*, 1952, No. 77). The author describes the design, construction, and standardization of pattern and corebox equipment for modern foundries.

The types of pattern mentioned are interchangeable, since at least four foundries are supplied with identical patterns.

**Measurement of Castability by Means of a Spiral Mould.** P. Schneider. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 379–381). A mould constructed in accordance with the Cronin mask method is described; it enables castability to be determined with great precision. It is suitable for light alloys as well as for cast iron and heavy alloys.

**The Randupson Process for Moulding in the Production of Steel and Bronze Castings.** G. L. Hancock. (*J. Trans. Soc. Eng.*, 1952, **43**, Jan.–Mar., 23–37). The Randupson process, with cement–sand moulds, shows considerable economies in capital expenditure since mould-drying stoves are eliminated. Once the technique of pattern preparation has been acquired subsequent work can be carried out by unskilled labour. Details are given of the moulding and casting technique together with the production methods of a large foundry making castings of up to 8 tons. Examples of the type of casting produced are shown.—B. G. B.

**Feeders for Hand Moulding.** (*Fonderie*, 1951, Oct., 2657–2658). Defects in castings are often caused by bad attachment of feeder heads due to insufficient flaring of the feeder-head base. One way of overcoming this is to use patterns in two halves. the fastening being formed by a core, When moulding, the core print is placed on the pattern and the feeder head is centred on this print. The core must be well keyed into the mould.—R. S.

**Application of Chills to Increase the Feeding Range of Risers.** E. T. Myskowski, H. F. Bishop, and W. S. Pellini. (*Amer. Found. Soc. Preprint*, 1952, No. 66). For castings of 0·25–0·35% carbon steel the maximum distance $D$ in inches which can be made sound with only one riser can be calculated by the formulæ

$$D \text{ (for plates)} = 4\tfrac{1}{2}T + 2$$
$$D \text{ (for bars)} = 6\sqrt{T} + T$$

where $T$ is the casting thickness. Chills placed between risers promote soundness for a distance of $2D$.—E. T. L.

**High Pressure Risers for Metal Economy.** J. Kraus. (*Hutnik* (Prague), 1952, **2**, Feb., 31–37). [In Czech]. Methods of using high-pressure risers on castings and the savings of metal attainable are discussed. Details of their construction and data, and graphs relating to the solidification of castings of various shapes when these risers are used are given.—P. F.

**Veining Tendencies of Cores.** (*Amer. Found. Soc. Preprint*, 1952, No. 6). The Sand Division Committee 8-J has shown that veining is caused by the choice of base sands, binders, metal pouring temperature, degree of ramming, degree of baking, the percentage of binders, and, in some cases, moisture. There is no test which enables the veining tendency of cores to be ascertained.—E. T. L.

**Core Boxes from Core Plugs.** J. N. Mathias. (*Amer. Found. Soc. Preprint*, 1952, No. 7). The author outlines the advantages of developing aluminium core boxes from wood or metal master core plugs, and then gives details of the methods of using a single-gang dump box and single-gang split box with open end.—E. T. L.

**The Use of Inserts in Making Large Cores.** E. Ježek. (*Hutnik* (Prague), 1952, **2**, Feb., 42). [In Czech]. A new method of employing steel or aluminium inserts in making large cores is described. A considerable saving in labour and weight is attained without sacrifice of quality.—P. F.

**Anhydrous Core Mixtures.** E. I. Kolotilin. (*Hutnik* (Prague), 1952, **2**, Feb., 40–41). [In Czech]. The composition, wet compression strength, dry tensile strength, preparation, and other physical properties of anhydrous core mixtures for ferrous castings, as well as the strength/drying-time curves, are given.—P. F.

**Study of the Utilization of Infra-Red Radiation for Drying Moulds, and Baking Cores.** (*Fonderie*, 1951, Oct., 2659–2664). To evaluate the efficiency of infra-red drying for moulds and cores, a small stove was used with thin, polished aluminium walls fitted with five infra-red 1250-W. lamps for a working surface of 18 sq. dm. (70 watts per dm.) emitting waves between 1·2 and 1·6μ. A mould containing sand 12 cm. deep was subjected to radiation. Thermocouples were fixed at various depths in the sand. Drying was continued until it was complete to a depth of 6 cm. Details are given for surface and depth drying, power consumption, and the heat used for water evaporation, and heating the sand and the moulding box. The study shows the difficulties of deep drying by infra-red rays. Low penetration of opaque bodies by infra-red rays means that all the energy is absorbed in the surface zone. It is difficult to dry cores of varying section due to shadows thrown by one core on another. To eliminate these shadows complex stove design is necessary. Otherwise the cores must be spaced at greater distances from each other which lowers the efficiency. Advantages of infra-red drying are: Energy is concentrated directly on the surface where it is required; the stove atmosphere does not interfere; elimination of thermal inertia losses gives, at first, a higher yield than that of an electrical convection stove; and more uniform drying.

**Allocation of Time for Manual Core Making in Core Boxes for Small and Medium Serial Production.** M. Skarbinski. (*Przeglad Odlewnictwa*, 1952, **2**, Mar., 71–78). [In Polish]. The problems of coremaking with special reference to the timing of individual operations are discussed.—V. G.

**How to Make Successfully a Three-Grooved Pulley.** G. Hénon. (*Fonderie*, 1951, Oct., 2653–2656). Reference is made to the American Foundrymen's Society's studies of the manufacture of a three-grooved pulley. The present article deals with the metallurgical aspect of the problem. Advantages and disadvantages of various types of iron are listed and details of melting procedure are given.—R. S.

**A Tricky Casting Job—Cast-Iron Basin with Built-in Metallic Elements.** (*Fonderie*, 1952, Jan., 2774–2778). The procedure of casting a special cast-iron basin, weighing 5 tons, steam-heated, for the chemical industry, is described. The basin has a flange in the upper portion 70 × 120 mm., a cylinder of 1860 mm. outside dia. and 80-mm. wall thickness, a convex bottom, five bosses, and some tubing. The pattern making and moulding are described.—R. S.

**Results Obtained in the Determination, with Resistance Strain Gauges, of Residual Stresses in Centrifugal Casting Moulds.** H. Bühler and W. Schreiber. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 297–301). The authors describe the technique for measuring residual stresses in moulds by means of resistance strain gauges, and discuss its advantages and difficulties. Results of measurements in cast-iron moulds are quoted.—J. G. W.

**Residual Stresses in and Life of Centrifugal Casting Moulds.** H. Bühler. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 303–309). The author reviews the problem of residual stresses in centrifugal casting moulds and their connection with mould life. Results of measurements taken over a number of years enable the author to recommend procedures and manufacturing methods which improve their life.—J. G. W.

**Centrifugal Casting of Molten Metals.** J. Kieswetter. (*Hutnické Listy*, 1951, **6**, Aug., 369–376, Sept., 425–428). [In Czech]. A detailed theoretical treatment of the main problems of centrifugal casting is given. On the basis of hydraulic phenomena occurring in the process, instructions are drawn up for the preparation of moulds, and the determination of the optimum speed of rotation. Attention is drawn to the importance of correct positioning of the mould cavity with respect to the metal feed, and the correct preparation and placing of vents. The solution of these problems is obtained with reference to the shape of the surface of the rotating molten metal.—P. F.

**Precision Casting.** M. Pomey. (*Microtecnic*, 1951, **5**, Nov.–Dec., 325–343). The principle and method of precision casting using the lost-wax technique are discussed in detail.

**Investment Casting from Frozen Mercury Patterns as a Means of Reproducing Pieces that are too Intricate for Other Methods.** (*Precision Met. Mold.*, 1952, **10**, Jan., 65–71). A description is given of the Mercast process of investment casting where frozen mercury is used as a disposable pattern rather than wax or plastic.—D. H.

**Further Mechanical Aids for the Foundry.** A. S. Beech. (*Proc. Inst. Mech. Eng.*, 1951, **165**, 27–41: *Found. Trade J.*, 1952, **92**, Mar. 13, 279–283; Mar. 27, 331–335). This survey covers devices introduced between 1942 and 1949. These include special moulding-machine layouts, brake-block production, knocking-out, sand treatment, and a multiple-belt storage hopper. In jobbing foundries jolt machines and sand rammers reduce the labour and make founding more attractive to apprentices.—E. T. L.

**Devices to Aid Casting Single-Handed.** (*Fonderie*, 1952, **73**, Feb., 2810–2814). The advantages of monorails, and mobile overhead trolleys for moving ladles and methods of lifting them are discussed.—R. S.

**Maintenance in Foundries in the U.S.S.R.** B. Počta. (*Hutnik* (Prague), 1952, **2**, Feb., 26–28). [In Czech]. The principles

on which the organization of maintenance work in foundries and other maintenance work in foundries and other metallurgical plants in the U.S.S.R. are based are explained, and economic features are discussed.—P. F.

**Hadfields (W. A.) (1934) Ltd.** (*Australian Found. Trade J.*, 1952, **3,** Feb. 17). A very brief description is given of this foundry situated at Bassandean, Perth, Western Australia. Three basic electric furnaces of 4–5 tons' capacity, one acid electric furnace of 1½ tons' capacity, and a 5-cwt. rocking arc furnace produce steels and irons for a variety of forgings and castings.—P. M. C.

**The New Foundry Institute at Aachen.** E. Piwowarsky. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 249–252). The recently completed Institute for the teaching of and research into foundry technology at the Rhine-Westfalian Technical University, Aachen, is described by its director.—J. G. W.

**Cold Repair of Fractured Castings.** (*Coke Gas*, 1952, **14,** Mar., 109–110). The Metalock process for repairing cracks in heavy castings is described. The alloys of which the keys are made have a known tensile strength, and the correct number of keys must be used to restore the original strength of the casting. This repair service is operated by Metalock (Britain) Ltd.—T. E. D.

**Contribution to the Theory of Degassing Molten Metals *In Vacuo*.** L. Fekete. (*Acta Technica Academiae Scientiarum Hungaricae*, 33–49). [In German]. This paper reports investigations continuing the work of M. Verö (*see J. Iron Steel Inst.*, 1950, **166,** Oct., 157). It deals mainly with the problem of the removal of hydrogen from melts *in vacuo* or under reduced pressures. A graphical method is developed which facilitates the determination of the depth of the zone in which gas bubbles begin to form.—P. F.

**The Theory of the Degassing of Molten Metals.** J. Verö. (*Acta Technica Academiae Scientiarum Hungaricae*, 1950, **1,** 1, 130–155). (In Russian]. The occlusion of hydrogen by metals is discussed and formulæ representing general relationships between the amount of occluded hydrogen, its partial pressure, and the temperature of the metal are derived. The methods and mechanism of degassing metals are reviewed and the theoretical limits of degassing under different conditions are expressed by general formulæ. On theoretical grounds it is shown that the only practical method of degassing is by blowing an inert gas through the molten metal; in all other methods the diffusion of hydrogen through the metal is the controlling factor in the velocity of degassing.

**Vacuum Impregnation of Castings.** L. W. Hull. (*J. Met.*, 1952, **4,** Jan., 30–32). A description is given of methods of impregnating castings, particularly of light alloys, which involve removal under vacuum of air and moisture from the pores, followed by immersion under pressure in the impregnant. Similar methods are also used in the bonding of steel and plastics, and steel and aluminium.—G. F.

**Internal Porosity in Gray Iron Castings.** J. C. Hamaker, jun., W. P. Wood, and F. R. Rote. (*Amer. Found. Soc. Preprint*, 1952, No. 23). The influence of phosphorus and alloying metals on the internal shrinkage porosity in a 3·25% C, 2·25% Si grey iron was determined by precision density measurements. Molybdenum causes greatest shrinkage, whilst nickel has only a small effect. The porosity of a Ni–Cr–Mo iron increased on adding phosphorus. Variation of carbon or silicon content had negligible effect. Metallographic studies showed that both molybdenum and chromium segregate strongly to the phosphide eutectic, thus altering the phosphide solidification and causing a drastic increase in contraction.

**Shrinkage and Piping.** E. Knipp. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 349–353). The connection between shrinkage and piping is considered theoretically, whence it is shown that the greater the cooling rate and the higher the shrinkage coefficient of the fluid in relation to the solid metal, the greater the pipe. Experiments relating silicon content to the ability to fill a mould, and to maximum castability, density, and piping were performed. The maximum castability occurs at the eutectic; density appears to be independent of silicon content, but is strongly influenced by the wall thickness of the castings. Piping increases with silicon contents greater than the eutectic composition, but is suppressed by high pouring temperature and slow pouring; the reverse is the case with basic electric steel.—J. G. W.

**Bruinell Fluxes and Anti-Piping Compounds.** (*Australian Found. Trade J.*, 1952, **3,** Feb., 13). This short article recommends 'Bruinella' E2 and E3 fluxes for cleaning and generally improving cast-iron quality, and E1 (exothermic) and Apece B (endothermic) compounds for improving the yield from steel ingots.—P. M. C.

**Applied Waste Control Principles.** J. R. Walley. (*Amer. Found. Soc. Preprint*, 1952, No. 53). The author deals with the detection and prevention of waste in the foundry.—E. T. L.

**A Test for Hot Tearing Tendency.** E. A. Lange and R. W. Heine. (*Amer. Found. Soc. Preprint*, 1952, No. 14). Rupture of the metal occurs locally due to the overstressing of the cooling and contracting metal. Evaluation of the principal factors responsible is difficult, and an empirical test is needed. Such a test, involving a horizontal rod cast in a sand mould, is described. One end of the rod is fixed and the other operates a dial gauge as the rod contracts. The results show that in white irons hot tearing strength and contraction rate decrease with increasing carbon content. Under restraint during cooling, the test casting elongates. Hot tearing occurs while the last 10% of the metal is freezing.—E. T. L.

**Metallurgy and Mechanics of Hot Tearing.** H. F. Bishop, C. G. Ackerlind, and W. S. Pellini. (*Amer. Found. Soc. Preprint*, 1952, No. 65). Studies at the time of hot tearing, using simultaneous radiography and thermal analysis of solidifying castings, showed that hot tearing occurs at near solidus temperatures when solidification is substantially complete, except for liquid films. A theory is developed to explain hot tearing in terms of hot-spot formation and solid contraction. This indicates that the pouring temperature should be considered as very critical with each type of casting.—E. T. L.

**The Influence of Foreign Nuclei on the Crystallization of Metals and Alloys, Particularly on the Formation of the Eutectic in Cast Iron.** W. Patterson. (*Giesserei Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 355–378). The author concludes that spontaneous nucleation in the absence of foreign nuclei occurs only after very appreciable undercooling of metals. In industrial alloys the structure as cast is determined by the number and type of foreign nuclei which become active at various stages of undercooling. (50 references).—J. G. W.

**Dust Problems in Foundries.** W. B. Lawrie. (*Foundry Trade J.*, 1952, **92,** Apr. 10, 379–384; Apr. 17, 421–423). The author considered the steps taken to reduce the silica dusts in the air, arising, for instance, from burning-on. The use of non-siliceous dusts for facing powder was not a complete success, but a flux-injected oxygen burner seemed to be a promising substitute for the pneumatic chisel. Dust masks, though uncomfortable, are now much improved and useful.

**Glass Bags Clean California Air.** P. Siechert and H. B. Menardi. (*Iron Age*, 1952, **169,** Jan. 24, 78–80). Smoke control equipment installed at a grey iron foundry in Alhambra, California, is described. Cupola gases are first cooled from 2150° F. to 1100° F. with recirculated air from cooling flues which further cool the gases to 420° F. Gases are then drawn through silicone-impregnated glass cloth bags which have an expected life of two years.—A. M. F.

**The Problem of Dust Removal and Ventilation in Foundries.** W. Mulhrad. (*Fonderie*, 1951, Nov., 2671–2684). The nature of foundry dust is discussed and the sources of emission are examined. The principles of dust-removal equipment are explained and various dust extractors and hoods are illustrated.—R. S.

**Inspection of Rejects, Recognition and Classification of Casting Faults.** F. Barheine. (*Giesserei*, 1952, **39,** Apr. 3, 157–163). Seventeen types of fault found in castings are described, their origins indicated, and their causes discussed in detail.—J. G. W.

## HEATING FURNACES AND SOAKING PITS

**The Heating of Steel Ingots.** G. Grenier. (*Echo Mines*, 1951, Nov., 601–604; Dec., 668; 1952, Jan., 33–35; Feb., 95–98; Mar., 177–179; Apr., 249–250). A general survey of the world's production of steel ingots is followed by details of unheated soaking pits. Advantages and disadvantages are enumerated. The uses of fuels in heated soaking pits, including coal, producer gas, coke-oven gas, and blast-furnace gas, are compared. The designs of furnaces are illustrated. Regenerators and recuperators are compared and examples are given, including details of carborundum recuperators. The importance of the reheating cycle is emphasized, especially

when working with special steels. Examples of tunnel furnaces with preheating chambers are given, and the conditions for oxidation or carburization from the furnace atmosphere are outlined. The historical development of heated soaking pits is followed, and various recent designs are illustrated. Combustion air preheating is mentioned. 'Stein' soaking pits are described, and some operating data are given, including gas consumption, temperatures, and soaking time.—T. E. D.

**Design and Operation of Modern Soaking Pits.** O. J. Stebel. (*Stahl u. Eisen*, 1952, **72**, Apr. 24, 466–475). The development of the design and operation of soaking pits, particularly in America during recent years, is reviewed, and the following conclusions are drawn: (1) A tight-fitting cover is indispensable and a limited number of burners facilitates construction. These should be placed so that there is a uniform temperature distribution whatever the charge but with no danger of burning any ingot. (2) In order to preserve good heat economy there should be automatic controls of the heating process, furnace pressure, and gas–air ratio. (3) Avoidance of burning necessitates a fuel with low calorific value. (4) Working so that the ingots are covered with a solid instead of a liquid scale offers such great advantages that it should be weighed against the greater working space thereby made necessary. (5) The greater heat loss from the large soaking pit can be kept within tolerable limits by good insulation. (6) Heat consumption with a cold charge heated to 1200–1250° C. should not exceed 400 kg.cal./kg. (7) Trouble-free operation of a soaking pit depends on the susceptibility to damage of its components. It is therefore necessary that the ancillaries such as cover carriage, recuperators, control gear, and fans, should be very reliable. (8) The pit should be made so that the ingots can be removed and sent forward to the mill in the order in which they come from the casting pit without undue delay, and its size should be related to the capacity of the mill.—J. P.

**High Temperature, High Speed Heating for Steel Rounds.** A. F. Kritscher. (*Iron Steel Eng.*, 1952, **29**, Mar., 55–60) The author describes the principles underlying high-speed heating of rounds for making seamless pipe and tubing and discusses the work done by the National Tube Co. in developing this. Tests are described which led to the installation of a high-temperature high-speed furnace at the Gary works in conjunction with a new seamless mill. Technical and operational data on the furnace are given.—M. D. J. B.

**Heat Flow Problems: Outline of the Relaxation Method of Calculation.** L. F. Daws. (*Iron Steel*, 1952, **25**, Feb., 65–68; Mar., 102–106). The author quotes simple examples to illustrate the fundamentals of Southwell's relaxation method of calculation and its application to heat-flow problems involving differential equations which can be transformed into sets of simultaneous algebraic equations. A particular example of a steady state heat-flow problem is worked out, in which the temperature distribution is required in a cylindrical ingot maintained at constant temperature at one end and over its curved surface, while the other end is cooling to ambient temperature. The technique for the study of the unsteady state heat-flow problem is explained in detail, and suggestions are made as to the conditions in which the method can be most helpful.—G. F.

**Induction Heating Ups Production of Bolt Manufacturing.** H. E. Jackson. (*Indust. Heating*, 1952, **19**, Feb., 254–260, 328). Comparison of the formerly used oil-fired furnace and the recently installed induction heater shows a 150% increase in production. The processing of bolts is described in detail. Induction heating allows controlled and uniform heating, with lower maintenance costs.—B. G. B.

**Contribution to the Analytical and Experimental Study of the Variation of Temperature in Electric Furnaces as a Function of Time and of the Power of the Furnace.** M. Billy and J. Brefort. (*Chaleur et Ind.*, 1952, **33**, Apr., 98–106). Previous theories are discussed and the results of experimental trials are treated mathematically.—T. E. D.

**Industrial Applications of Semi-Conductors. 2: Silicon Carbide Resistors.** R. W. Sillars. (*Research*, 1952, **5**, Apr., 169–175). Silicon carbide crystals which have been sintered together at extremely high temperatures form a semi-conducting mass that obeys Ohm's law, and is used for resistance heating, especially of furnaces. Granular silicon carbide displays a non-linear relation between current and voltage.—C. J. B. F.

## HEAT-TREATMENT AND HEAT-TREATMENT FURNACES

**A Comparative Study of Heat-Treatment Processes for Steel, and Their Definition.** W. Grundig. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, July, 283–320). [In Portuguese]. On the basis of microstructures occurring in heat-treated steels, the author defines the various heat-treatments and the structures associated with them. The kinetics of the transformation of austenite and martensite and the intermediate structures obtained by isothermal treatments are reviewed.—R. S.

**Rocket Parts Effectively Heat Treated in Mechanized Salt Bath Furnace.** K. Rose. (*Mat. Methods*, 1952, **35**, Jan., 90, 91). A brief account is given of the automatic salt-bath heat-treating cycle for small rocket motor bodies at the Lansing plant of Oldsmobile, General Motors. The parts are about 8 in. long, 2 in. in dia., and $\frac{1}{8}$ in. wall thickness. The material is steel SAE 4140 which is heated and quenched to just above the martensite transformation temperature.—P. M. C.

**Influence of Dimensions, Pre-treatment and Hardening Medium on the Depth of Hardening of Unalloyed Tool Steels.** E. Theis. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 113–118). The influence of dimensions, type of hot-working, heat-treatment, nature of water used for quenching, surface condition, and type of hardening furnace on the depth of hardening has been investigated with tool steels (0·6–1·0% C, 0·2–0·6% Mn, 0·1–0·2% Cr). In general, the effect of these variables was small, but in order to obtain the best and most uniform results in testing the hardenability of tool steels the most suitable specimen is one with a 20 × 20 mm. cross-section, annealed or normalized and pickled, and hardened from a salt bath.—J. P.

**Production Heat Treating.** G. Goepfert. (*Steel*, 1952, **130**, Feb. 11, 82–84). **Production Heat-Treatment of Ross Automotive Steering Assemblies.** G. Goepfert. (*Indust. Heating*, 1952, **19**, Mar., 408–424, 571). **Heat-Treating Automotive Steering Assemblies.** G. Goepfert. (*Steel Processing*, 1952, **38**, Feb., 82–87, 101). The carburizing, dry cyaniding, and clean hardening of various parts of automobile steering assemblies involve heat-treating under critical conditions and controlled atmosphere. By integrating plating and mechanical cleaning operations with the heat-treatment, one plant is producing 850,000 lb. of parts per month.—A. M. F.

**Flame-Hardening of Locomotive Tyres.** (*Railway Gaz.*, 1952, **96**, Apr. 4, 376–377). As a result of experiments on the problem of reducing flange wear, the Peddinghaus organization is now manufacturing a semi-automatic plant for flame-hardening locomotive wheel flanges, a feature of which is the use of oxygen and town gas as the heating medium. It is claimed that the life of a tyre of one type of locomotive was approximately 107,000 miles with an unhardened flange; this was increased to 214,200 miles when the flange was flame-hardened. It is also claimed that flame-hardened tyres do not wear the track as much as normal tyres.—J. P. S.

**Which Surface Hardening Process?** L. Spencer. (*Product Eng.*, 1951, **22**, Aug., 157–162). Case carburizing, nitriding, and flame hardening are compared and the processes are described. A detailed reference chart is given as an aid to selection of the right method and in this details are given of the hardness range, depth of case, typical applications, steels used, and heat-treatment as well as relative advantages and disadvantages.—A. M. F.

**Induction Hardening in Malleable Iron Casting.** A. Rühenbeck. (*Giesserei*, 1952, **39**, Mar. 6, 103–107). With the aid of induction surface hardening, malleable iron castings can often serve as substitutes for forgings. Details of treatments for both white- and black-heart irons are given and the economic aspects are considered.—J. G. W.

**Induction Heating Equipment.** (*Machine Shop Mag.*, 1952, **13**, Jan., 27–32). Induction heating machines which utilize radio-frequency power are described. Single-purpose machines are only warranted where quantity production is involved. Short runs of components having different sizes and shapes are more suitably processed in semi-automatic machines with a universal workhead. Surface hardening, tempering, and annealing may be carried out locally or on a complete component, as well as soldering, brazing, and melting. Four types of machine are illustrated and their operation described.

**Vertical Bell-Type Furnaces for Coiled Strip.** (*Iron Coal Trades Rev.*, 1952, **164**, Feb. 15, 385). This article briefly describes the six new vertical cylindrical bell-type annealing

furnaces supplied by the General Electric Co., Ltd., to the Brierley Hill works of Richard Thomas and Baldwins, Ltd. Each is rated at 36 kW. and has its elements in two circuits, one being automatically switched off just before the desired temperature is reached. They are capable of annealing 700 tons per week of coiled silicon steel strip.—G. F.

**Induction Hardening of Crankshaft Journals.** T. Bishop. (*Metal Treatment and Drop Forg.*, 1952, **19**, Mar., 131–134). The equipment in use at Ambrose Shardlow and Co. Ltd., of Sheffield, is described. Four modern Tocco units are employed for treating 63-lb., 7-bearing, 6-throw crankshafts at the rate of 17/hr. An older tunnel-line unit by EFCO is also described. The production on this unit is only 7/hr., but it can be altered to accommodate different jobs much more quickly than the Tocco.—P. M. C.

**Special Gas-Fired Stress Relieving Furnaces Used in Manufacture of Large Processing Equipment.** (*Indust. Heating*, 1952, **19**, Mar., 462–470, 572–573). To relieve stress after welding, carefully controlled heat-treatment processes are carried out. These are followed by visual and X-ray inspection and annealing in a gas-fired furnace. An example is cited of a vessel too large to go in existing equipment, which was stress relieved by covering with asbestos and heating by a gas-fired blower. Special treatment of long (*e.g.*, 57-ft.) vessels by heating in sections is described. Accounts are also given of heat-treating stainless steels.—B. G. B.

**Large Electrical Resistance Furnaces.** J. Arens. (*Elektrowärme Techn.*, 1952, **3**, Apr., 27–33). This is an illustrated account of the application and scope of large resistance furnaces in metallurgical manufacturing processes such as stress-relieving of steel tubes, bright-annealing, and tinning.

**Work on Standards in the Field of Resistance Furnaces** (*Elektrowärme Techn.*, 1952, **3**, Feb., 6–8). The problem of standards for electric resistance furnaces is discussed, with reference to work done during the war (1939–45) and present-day needs.—P. F.

**An Investigation of the Quenching Characteristics of a Salt Bath.** M. J. Sinnott and J. C. Shyne. (National Metal Congress, Detroit: *Indust. Heating*, 1952, **19**, Feb., 236–240). Stainless steel bars were quenched from 1550° F. into unagitated salt baths held at 385–725° F.; the experimental technique is described. From temperature data obtained and physical properties of the steel, the Grossman severity of the quench was determined; it was comparable with those reported for oil quenching with agitation. Variations in the severity of the quench are shown to be due to the existence of a surface film resistance. The surface heat-transfer coefficients were calculated.—B. G. B.

## FORGING, STAMPING, DRAWING AND PRESSING

**Some Leading Developments in European Forging Equipment.** P. Granby. (*Steel Processing*, 1952, **38**, Feb., 63–67, 81). Several post-war designs of upsetters and mechanical forging presses are briefly described. The author emphasizes the progress made by German firms.—P. M. C.

**High-Power Bending and Forging Machine.** (*Railway Gaz.*, 1952, **96**, Apr. 18, 431). Joshua Bigwood and Son, Ltd., have built a horizontal reciprocating bulldozer, for hot or cold shearing and forming operations, in conformity with the following data: Capacity: 300 tons end pressure; speed: 10 strokes/min.; stroke: 32 in.; die space with crosshead forward: 48 in.; crosshead face area: 72 × 24 in.; motor: 30 h.p. at 940 r.p.m. Special features in its design are briefly described.—T. E. D.

**600/3000-Ton Forging Presses.** (*Engineering*, 1952, **173**, Apr. 18, 489). The presses, ranging from 600 to 3000 tons, introduced recently by Wilkins and Mitchell, Ltd., of Darlaston, Staffordshire, are described. They are designed to allow multiple operations, using up to four sets of dies. High rates and accurate forgings are achieved. Brief technical and operational details are given.—M. D. J. B.

**Improvements in Die Forging Technique.** F. Drastík. (*Hutník* (Prague), 1952, **2**, Feb., 42–45). [In Czech]. An illustrated account of methods and suggestions for improving the production of die-forged parts are given.—P. F.

**How Forged Rolls Are Made.** (*Hutník* (Prague), 1952, **2**, Mar., 66–68). [In Czech]. Metallurgical principles and works technique involved in making forged steel rolls containing 0·85% Al, 1·1% C, and 1–2% Cr are discussed. Sources of damage and their elimination are considered.—P. F.

**A Study of Some Impacts Between Metal Bodies by a Piezo-Electric Method.** A. W. Crook. (*Proc. Roy. Soc.*, 1952, 212A, May, 377–390). Continuous measurement of the force throughout impacts between metal bodies is described. Within their appropriate ranges, the theories of elastic impacts due to St. Venant and Hertz have been confirmed. For impacts so hard that the elastic regime preceding the deformation may be neglected the experimental results agree closely with force–time curves calculated, assuming that deformation is opposed by a constant pressure. This dynamic flow pressure is greater than the similarly defined pressure experienced in static tests and the difference cannot be accounted for in terms of forces of a viscous type.—B. G. B.

**Rubber Reduces Foundation Costs.** (*Torque*, 1952, **1**, Apr., 3–5). The use of rubber-bonded-to-metal anti-vibration mountings manufactured by the Andre Rubber Co., Ltd. in setting up a Bliss press weighing 8¼ tons, for George Glover and Co., is described. Total cost was £42, compared with £300–£400 for the more usual concrete block with resilient underlayer.—T. E. D.

**Stretch-Forming.** R. Wood. (*Aircraft Prod.*, 1952, **14**, Mar., 77–84; Apr., 116–123). The mechanical details and method of operation of the Sheridan longitudinal stretching machine are described. Panels 22 ft. by 5 ft. can be formed. Tooling methods and examples of forming procedure are described and illustrated.—T. E. D.

**Rotary Stretch-Forming.** (*Aircraft Prod.*, 1952, **14**, May, 183–184). The mode of operation of the Bath radial draw-forming machine is described. It can be used for forming high-alloy gas-turbine components. Elliptical or rectangular bends can be produced. Six sizes of machine are available from 12½ to 100-ton capacity.—T. E. D.

**Cold Pressing of Steel.** J. Lomas. (*Brit. Steelmaker*, 1952, **18**, Jan., 28–33). After describing the general characteristics of mechanical and hydraulic presses, the author discusses the types of steel which are suitable for cold pressing, the metallurgy of the process, and the various treatments required to ensure a satisfactory product.—G. F.

**Some Practical Hints on Special Die Design.** F. Strasser. (*Sheet Metal Ind.*, 1952, **29**, Mar., 230–234, 236). The article presents some practical suggestions and simple solutions to problems encountered in practice, as an aid in designing and building small special dies.—P. M. C.

**Latest Developments in Extrusion of Metals.** E. Loewy. (*Iron Steel Eng.*, 1952, **29**, Apr., 65–69). After a brief review on the development of metal extrusion the author considers in detail the hot extrusion of steel. Information is given on press design, and types of steel for extrusion and dies. Reference is made to the extrusion of 18/13 stainless steel tubing, and some non-ferrous metals.—M. D. J. B.

**The Influence of Length on the Phenomenon of Semi-Fragile Tearing.** H. de Leiris. (*Génie Civil*, 1952, **129**, Apr., 154). A few drawing experiments were performed at several temperatures on long and short specimens of mild steel. The results indicate that long specimens fracture more easily than short specimens.—T. E. D.

**Sensitive Comparator for Measuring Variation in Diameter of Wires.** J. C. Evans, R. S. Marriner, and I. G. Morgan. (National Physical Laboratory: *Engineering*, 1952, **173**, Apr. 25, 529–530: *Machinery*, 1952, **80**, Apr. 24, 735–739, 744: *Machinist*, 1952, **96**, May 3, 679–682). This article describes a sensitive comparator suitable for measuring the variation in diameter of wires down to 0·001 in. For local readings, the comparator may be fitted with a dial indicator; alternatively, it can be fitted with an amplifier and recorder giving a continuous record of variation as wire is drawn through the measuring head.—M. D. J. B.

**Friction, Wear, and Lubrication in Wire Drawing.** W. Papsdorf. (*Stahl u. Eisen*, 1952, **72**, Apr. 10, 393–399). Modern ideas on friction and classification of various types are presented. Lubrication in wire drawing falls within the category of boundary lubrication. The dependence of the coefficient of friction on sliding speed and pressure is shown diagrammatically and modern concepts regarding wear are compared with the behaviour of dies during drawing. The chemical and physical differences between fatty and mineral oils are explained; the smaller pressure and temperature dependence of viscosity of the former make them particularly suitable for use under conditions of varying temperature and pressure and as additives to high-pressure lubricants. The important part played in wire drawing by lubricant carriers,

such as lime, borax, and phosphate films, is indicated and the necessity for correct ratio of lime to soap as an aid to good drawing is stressed. Finally, curves are given illustrating the variation of coefficient of viscosity of 24 lubricant mixtures with pressure, up to 280 kg./sq. mm.—J. P.

**Lubricants and Lubricant Carriers in Drawing Steel Wire. I.** W. Lueg and K. H. Treptow. (*Stahl u. Eisen*, 1952, **72**, Apr. 10, 399–412). The lubrication conditions in a drawing die are examined and shown to be a special case of boundary lubrication. The drawing force has been measured, during successive passes, on patented steel wire using a variety of lubricants and carriers comprising oils, greases, and some solid lubricants (graphite, molybdenum sulphide, and soap) and lime, borax, graphite, and alkali, respectively. From the results, the value of the coefficient of friction $\mu$ was calculated and plotted as a function of mean surface pressure. The maximum number of drafts obtained before failure of the lubricant was also observed. In contrast with previous data, which indicated that, for a given lubricant, $\mu$ varied only within certain limits, these tests have shown that $\mu$ rises progressively with increasing mean pressure. In ten successive drafts, when the pressure rose from 110 to 240 kg./sq. mm., $\mu$ increased from 0·035 to 0·165 in unfavourable, and from 0·03 to 0·06 in favourable, instances. This increase is more or less pronounced according to the particular lubricant-carrier combination employed. The curves of $\mu$ against mean surface pressure sometimes cross so that one pair has the better lubricating power at low pressures and the other pair at high pressures. By using alkali as a carrier with solid or liquid lubricants, marked reductions of $\mu$ and improved finish of the drawn wire were obtained. From these results some conclusions are drawn as to the lubrication processes in the die.—J. P.

## ROLLING-MILL PRACTICE

**The New Blooming Mill at Donawitz, Its Equipment and Operation.** A. Vacek. (*Stahl u. Eisen*, 1952, **72**, Mar. 13, 291–296). The new blooming mill is very powerful and constructed on modern principles. Its important characteristics are: (1) Individual drives to the upper and lower rolls, which reduces starting torque and improves the efficiency of D.C. motors; (2) application of Amplidyne generators for speed control of roll motors and for excitation of the control generators; (3) use of D.C. motors with Amplidyne machines for the more important auxiliary drives. The auxiliary drives are over-rated at present and the power consumption per ton of steel is therefore greater than on a former mill. The soaking pits are to be rebuilt in 1952. They will each have an individual recuperator and the design is illustrated.—J. P.

**New Austrian Steelworks Plant.** (*Iron Coal Trades Rev.*, 1952, **164**, Mar. 28, 713–716). This article gives details of new rolling-mill installations, including a 10-stand hot mill and a 4-high reversing cold mill, at the Austrian steel plants at Donawitz and Krieglach.—G. F.

**A Wheel Mill at Sheffield.** (*Engineer*, 1952, **193**, Apr. 25, 574–576). **Railway Wheel Mill of Messrs. Steel, Peech and Tozer, Sheffield.** (*Engineering*, 1952, **173**, Apr. 25, 515–517). **Steel, Peech and Tozer Railway Wheel Mill.** (*Machinery*, 1952, **80**, May 15, 857–860). **Modern Practice in Steel Wheel and Disc Production.** (*Iron Coal Trades Rev.*, 1952, **164**, May 2, 983–985). **Wheel Mill at the Works of Steel, Peech and Tozer.** (*Brit. Steelmaker*, 1952, **18**, May, 216–217, 221). **Continuous Process Wheel Rolling Mill.** (*Railway Gaz.*, 1952, **96**, May 2, 489–492). The article describes the new wheel mill at the works of Steel, Peech and Tozer, Sheffield. The plant includes a double-acting ingot-breaking machine, a 6000-ton forging press, a wheel rolling mill, and a 1500-ton dishing press, with other ancillary equipment. The output is between 3000 and 3500 solid wheels per week.—M. D. J. B.

**Trostre Works: A Description of the Rolling Mills and Accessory Plant.** J. S. Gazard and G. E. Jones. (*Sheet Metal Ind.*, 1952, **29**, Mar., 198–210). This illustrated description of the Trostre works of the Steel Company of Wales includes layout, continuous pickling, 5-stand tandem cold mill, electrolytic cleaning, annealing gas plant, temper mills, shearing lines, and electrolytic tinning lines.—P. M. C.

**Operating and Economic Aspects of High Speed Tandem Cold Reduction Mills.** F. K. Schefe. (*Iron Steel Eng.*, 1952, **29**, Mar., 103–107). A detailed study is made of actual and theoretical mill capacities. It is suggested that high-speed tandem cold reduction mills rarely operate at over 50% efficiency. The reasons for this are discussed. The author groups delays under three headings: clearly defined delays; delays responsible for steady loss of production but which are often accepted as part of normal operations; and intermittent delays due to poor mill performance. The author suggests that the greatest single cause of lost operating time is in roll changes.—M. D. J. B.

**Design and Operation of a Cluster-Type Reversing Cold Rolling Mill with Fluid Drive.** M. Reimann. (*Stahl u. Eisen*, 1952, **72**, Apr. 10, 416–421). A cluster-type reversing mill with fluid drive has proved successful for the production of very thin cold-rolled strip. The oil pressure drive for mill and tension reels allows speed for a given pass to be changed continuously to that for another. Because of the small moving mass, the accelerating and braking are adequately short; the strip tension is uniform and variable over a very wide range, sufficient for all requirements. The strip produced on this mill is uniform and smooth and has a surface suitable for subsequent coating. A prerequisite for trouble-free working is a supply of metallurgically clean and uniform hot strip, with either a scale-free hot-rolled or a cold-rolled surface and clean edges.—J. P.

**Emergency Drive Arrangements for Blooming Mill Auxiliaries.** F. C. Fennell. (*Iron Steel Eng.*, 1952, **29**, Mar., 82–88). The author examines the three main types of emergency arrangements on mills: Emergency operation from one of the drive generators; provision of a standby generator and controller; and duplication of generators. The relative merits of these three main classes are discussed from the standpoint of initial equipment cost, installation cost, floor space requirements, maintenance, and performance under both normal and emergency operating conditions.—M. D. J. B.

## MACHINERY FOR IRON AND STEEL PLANT

**The Handling of Heavy and Awkward Loads in Mines and Works.** (*Echo Mines*, 1952, Mar., 188–190). The Traveloader hull, a multi-purpose handling vehicle, is illustrated and its various applications are described. Its chief advantage is in lifting and carrying long loads along the length of the truck by means of a lateral lifting fork and winch.—T. E. D.

**Application of Basic Principles in Planning Materials Handling Methods.** T. G. Lutz. (Industrial Management Soc.: *Blast Furn. Steel Plant*, 1952, **40**, Mar., 312–317). The author states and discusses the principles to be borne in mind when planning methods of moving materials.—J. P. S.

**Problems of Selecting Voltage for Steel Mill Power Distribution Systems.** D. L. Beeman. (*Blast Furn. Steel Plant*, 1952, **40**, Mar., 323–329). Where either 6·9 or 13·8 kV. is to be the main mill distribution voltage, then 13·8 kV. should be chosen. In steel mills, 34·5 kV. would be selected where it was desired to use indoor metal-enclosed switchgear in the circuits.—J. P. S.

**Efficiency of Mechanization in the Metal Industry.** F. S. Kasjanov. (*Hutník* (Prague), 1952, **2**, Apr., 83–86). [In Czech]. Mechanization and its economic aspects in Russian metal-producing and processing plants, with special reference to developments in steelworks and rolling mills over the last few years, are surveyed.—P. F.

**Modern Hydraulic Applications.** J. R. Carlson. (*Iron Steel Eng.*, 1952, **29**, Mar., 94–102). This paper is confined to the modern uses of oil hydraulics in motion and the manner in which this relatively new means of power transmission is being applied to solve complex problems for industry. Detailed descriptions of hydraulic applications are given relating to transmissions, hydraulic motors, absorption of power in braking devices, hydraulic lines for forging hammers, hydraulic traction drives, and drives for marine engines, plate stackers, and wire extruder drives.—M. D. J. B.

**Some Developments in Open-Hearth Charging Machines.** H. W. Ball. (*Iron Steel Eng.*, 1952, **29**, Apr., 90–93). After brief considerations on the design of open-hearth chargers, the author discusses the advantages of hydraulic chargers and gives a detailed description of a new crane consisting of a single 50-h.p., 850-r.p.m. motor driving a single hydraulic pump operating at 170 lb./sq. in. Details of controls, operator's compartment, and structural design are given.—M. D. J. B.

**Crane Limit Switch Failures.** C. H. Littlewood. (*Iron Steel Eng.*, 1952, **29**, Apr., 100–101). A brief description is given of actual crane limit-switch failures which have occurred in

steelworks. The reasons for these failures are discussed and suggestions are made for the improvement of these switches.

**Telescopic Ram Pit Cranes.** R. W. Harry. (*Iron Steel Eng.*, 1952, **29**, Apr., 94–98). Details are given of a telescopic ram soaking-pit crane constructed by the Alliance Machine Co. The mast consists of three progressively smaller sections which fit into each other. The chief advantage is that the crane can operate with less head room.—M. D. J. B.

**Plant and Processes at the Abbey Works of the Steel Company of Wales.** (*Elect. Rev.*, 1952, **150**, Feb. 22, 373–381). A general outline is given of the plant layout and processes in the Abbey melting shop of the Steel Company of Wales. The electrical equipment is discussed, of which the 135-ton cranes in the mixer and furnace bays, and the 300-ton crane in the casting bay are detailed. Material is fed into the steel furnace by a chariot which traverses the charger. Movement of the charger is by two 75-h.p. 220-V. D.C. motors in series across a 440-V. supply. Brief mention is made of the pig iron mixer equipment and the ancillary furnace installations.—H. D. W.

**Spring End Trucks on Steel Mill Cranes.** H. K. Hybarger. (*Iron Steel Eng.*, 1952, **29**, Apr., 102–103). A short description is given of spring-mounted end carriages for electric overhead travelling cranes. The spring mounting serves to cushion the crane and protect it, and all equipment, from shock and to reduce impact on the gantry. Although patented in 1925, few cranes have been designed on this principle. The author suggests that there may be considerable scope for this system.

**Has Industrial Tractor Design Kept Pace with Steel Mill Operating Requirements?** C. Lord. (*Iron Steel Eng.*, 1952, **29**, Mar., 75–80). Mechanical handling equipment used in the iron and steel industry in the U.S.A. is reviewed. The essential characteristics are discussed: namely, safety and robustness. Trends in modern design are examined.

**Gas Turbine Truck.** H. C. Hill. (*S.A.E. J.*, 1952, **60**, Jan., 29–33; Feb., 30–35). A 175-h.p. gas turbine developed by Boeing has in 12 months operated over 15,000 miles in a Kenworth truck. The first part of the article describes the rotor failures that occurred during field testing, and the developments made to overcome the troubles which were in the main due to vibration and excessive thermal stresses. The second instalment deals with general test results.—P. M. C.

**The Cause and Cure of Pulsation in Centrifugal Blowers.** O. W. Acheson. (*Indust. Heating*, 1952, **19**, Mar., 426–428). Modification to the blower design can be made if it is known that the blower will have to operate at a fraction of its rated volume. Suggestions to prevent pulsations in existing plant are given.—B. G. B.

## LUBRICANTS AND LUBRICATION

**Benefits of Modernized Lubrication in Steel Rolling Mills: Roll-Neck Bearings, Roller Tables and Mill Pinions.** P. W. Murray. (*Iron Coal Trades Rev.*, 1952, **164**, Feb. 29, 483–485). The author discusses the lubrication of roll-neck bearings, roller tables, and mill pinions, and indicates the savings in oil effected with modern enclosed gears as compared with open gears. The benefits derived from correct design and modern lubrication are summarized.—G. F.

**The Lubrication Engineer in Heavy Engineering: Modern Lubricating Systems in Steel-Rolling Mills.** S. Norton. (*Iron Coal Trades Rev.*, 1952, **164**, Feb. 15, 361–369). The author reviews modern lubrication practice on the heavier types of rolling mill and describes circulation systems for oil and grease lubrication of the different parts. The choice of lubricants for various purposes is discussed in some detail, and it is emphasized that the lubrication system should be taken into account in the early design stage of a mill.—G. F.

**The Lubricating Engineer and Organized Lubrication in the Steel Industry: Importance of Mechanical Efficiency in Securing Maximum Production.** G. D. Jordan. (*Iron Coal Trades Rev.*, 1952, **164**, Feb. 1, 251–256; Feb. 8, 319–324). The author describes the organization necessary to ensure mechanical efficiency in various items of plant, and discusses the status of the lubrication engineer, his work, and his relationship to the remainder of the organization. Attention is given to the storage of lubricants, and the importance of constant checking of lubricant consumption and quality is indicated. The design of lubrication systems, of both the batch and continuous by-pass types, is described, and the training of operatives is briefly considered.—G. F.

**Quality Control of Lubricants.** C. R. Burton. (*Iron Steel Eng.*, 1952, **29**, Apr., 59–63). This article describes routine tests carried out on lubricants to ensure that these are up to standard. Tests consist in taking oil samples daily from all equipment in continuous operation; the samples are then submitted to laboratory tests. The author shows how, by a rational approach to lubricating problems, some 65 oils and greases used in an iron-mining company were reduced to 12 lubricants.—M. D. J. B.

**The Nature of Soap-Thickened Lubricating Greases.** Marjorie J. Vold and R. D. Vold. (*J. Inst. Petroleum*, 1952, **38**, Mar., 155–163).

## WELDING AND FLAME-CUTTING

**Carbon Steels Successfully Welded by Inert-Gas-Shielded Metal Arc Process.** H. T. Herbst and T. McElrath, jun. (*Mat. Methods*, 1952, **35**, Feb., 86, 87). The authors describe the use of a new argon–oxygen mixture, containing approximately 5% oxygen, which permits welding at much higher speeds without undercutting, improves coalescence of the weld metal, and provides good stability and little spatter.—P. M. C.

**Gases and Non-Metallic Inclusions in Electric Arc Welding.** J. Maria Sistiaga. (*Ciencia y Tecnica de la Soldadura*, 1952, **2**, Jan.–Feb. [In Spanish]. The presence of porosity, the formation of nitrides, the nature and origin of some non-metallic inclusions in welds made with electrodes having an iron oxide base coating were studied. The effect of these inclusions on the mechanical properties of the weld metal is discussed.—R. S.

**Modern Steel Chain Manufacture: Production and Heat Treatment of Higher Tensile Short-Link Chain and Chain Slings.** W. G. Biggart. (*Iron Coal Trades Rev.*, 1952, **164**, Apr. 11, 807–815). The author gives a detailed description of the production of higher-tensile chain by resistance welding and flash butt-welding, and discusses the problems arising in the manufacture and heat-treatment. Mechanical tests are described and suggestions are made on the utilization of the higher safe-working loads of higher-tensile chains and chain slings. The assembly of all-steel slings, using atomic hydrogen welding, is also described.—G. F.

**Spot Welding of Coated Mild Steel Sheet.** A. J. Hipperson and P. M. Teanby. (*Welding Res.*, 1951, **5**, Dec., 275*r*–278*r*). Resistance welding was applied to the fabrication of cadmium and zinc-coated sheet steel assemblies to determine the effect of the coating on strength and weld quality. The deposits investigated were cadmium (0·0003 in.), zinc (0·0001 in.), and phosphated zinc (0·0001 in.). It was found that electrode sticking and sensitivity of spot weld size and quality to small changes of machine settings have an adverse effect. Acceptable welds were produced in all cases apart from phosphated zinc. Chromium–copper electrodes can be used for up to 500 welds.—U. E.

**Weldments Find Increased Use in Gear Drives.** C. J. Schorsch and R. Hirsch. (*Iron Steel Eng.*, 1952, **29**, Mar., 122–128). The authors describe the modern trend of using welded design in machine casings instead of cast iron or cast steel. This process simplifies foundry problems, makes for simpler and more efficient design, and reduces costs.—M. D. J. B.

**Surface Hardening and Deposition with and without Covered Electrodes.** A. W. Taylor. (*Ciencia y Tecnica de la Soldadura*, 1952, **2**, Jan.–Feb.). [In Spanish]. After describing the nature of hardness and strength of materials, the author states the properties conferred by the more common alloys and outlines surface-hardening methods. The importance of various electrode coatings for deposition of hard surfaces is explained.—R. S.

**Automatic Welding with Enclosed Arc at High Current Densities.** V. P. Demyantsevich. and I. A. Blokh. (*Avtog. Delo*, 1949, No. 9, 3–6). [In Russian]. An account is given of physical and metallographic investigations of the properties of weld metal and joints produced by the automatic submerged-arc butt-welding of steel at exceptionally high current densities. Densities up to 250 amp./sq. mm. were obtained with electrode wire 2–3 mm. in dia., the thermal concentration giving depths of penetration 1·5–2·5 times greater than those obtained normally. The macro- and microstructures of seams and adjoining areas are illustrated and dimensions and data are given on the hardness of the material at various points of welded specimens. The new technique is said to enable increased thicknesses to be welded without edge preparation, the design of automatic welding machines to be simplified, and economies in current consumption to be effected.—S. K.

**Experiments on Automatic Submerged-Arc Welding in Chemical Plant Construction.** L. G. Avrukh. (*Avtog. Delo*, 1949, No. 9, 18–19). [In Russian]. In the investigation described, 14-mm. plates of low-carbon steel were automatically welded with a submerged arc, and the effect of the flux on the quality of the joints obtained was determined. Two fluxes were used, both singly and mixed, the tensile strength, elongation, lateral contraction, and Brinell hardness of specimens being found for each case. Seam quality was seriously affected by insufficient edge preparation and clamping.

**Automatic Submerged-Arc Welding of Thin Steel.** M. Ya. Al'per and Z. A. Dobrotina. (*Avtog. Delo*, 1949, No. 9, 20–22). [In Russian]. Satisfactory results were obtained in the experimental investigation of the welding, with a submerged-arc and low-carbon steel electrode, of low-carbon steel sheet 2·5, 3·0, and 4·0 mm. thick. A titanium dioxide flux gave weld metal with a Brinell hardness of 187 (compared with 131 for the base metal), and tensile strength of 37–42 kg./sq. mm.

**VNITOS Conference on the Strength of Welded Structures.** N. N. Rykalin. (*Avtog. Delo*, 1949, No. 9, 32). [In Russian]. A brief review is given of the proceedings at the Moscow conference of the Welders' Technical Association, at which special attention was given to the effect of deformation during welding on the strength of welded structures. The following recommendations are made: (1) Permitted stresses in seams should be increased both for low-carbon steels and low-alloy structural steels; (2) the most important condition for joint strength is the absence of stress-concentrating irregularities; and (3) with proper design and technique internal stresses in the seam are not harmful.—S. K.

**Some Metallurgical Peculiarities of Automatic Welding at High Speeds.** B. I. Medovar. (*Avtog. Delo*, 1949, No. 11, 3–7). [In Russian]. An account is given of an investigation of the special features of the reaction between metal and slag when low-carbon steel 8–12 mm. thick is automatically welded at 120–150 m./hr. with a submerged arc of approximately 200 kW. Macro- and microstructures of such seams are considered in the light of information from the literature. Data are given on the effect of arc length and position of specimen on the transfer of silicon and manganese to the weld metal, and the effect of flux composition on the composition of the weld metal and on the mechanical properties of deposited metal at very high welding speeds.—S. K.

**Investigation on the Failure of Welded Pump Columns.** F. C. Johnson. (*J. S. African Inst. Mech. Eng.*, 1952, **1**, Jan., 151–155). Investigation of vibration and water hammer did not reveal excessive load, and tension and fatigue tests showed weld metal to be generally satisfactory. Faulty welds and bending stresses due to non-circularity are suggested causes of longitudinal weld failure.—H. R. M.

**X-Ray Testing of Welds for High-Pressure Vessels.** T. B. Johnston. (*Gas Times*, 1952, **70**, Feb. 22, 241–247). The technique used in detecting welding faults in high-pressure-gas apparatus by means of a 220-kV. Siemens Schuckert X-ray set is described.—T. E. D.

**Filler Metal for Edges of Boring Bits and Cutting Tools.** G. Vie. (*Echo Mines*, 1952, Jan., 37–38). Stellite, Stoodite, Alacrite, Haschrome, Haystellite, Borium, Adala, and composite rod are mentioned. Their compositions, properties, and methods of application are briefly outlined.—T. E. D.

**Welding as an Aid in the Foundry.** A. Markin. (*J. Inst. Australian Foundrymen*, 1950, **2**, 183–192). The article presents the practical difficulties associated with welding in the foundry. A classification of the available electrodes for welding various types of steel, cast iron, and several non-ferrous alloys is given, followed by suggestions as to their applications.—P. M. C.

**Reclamation of Iron Castings by Reinforced Bronze Welding.** G. G. Musted. (*Welding Metal Fab.*, 1952, **20**, Jan., 25–26). The author describes the repair and reclamation of defective iron castings for use under high pressure. The cracks are drilled at the ends and at intermediate positions, studs are screwed in, and sealing runs are electrically welded from stud to stud. The whole length is finally bronze welded with the oxy-acetylene flame.—U. E.

**Reconditioning Cast-Iron Rolls by Additions of Cast Metal.** R. Rolla and A. Colle. (*Met. Ital.*, 1952, **44**, Jan., 6–8). The repair of cast-iron mill rolls which have failed at the wobbler, neck, or near the roll is described. Welding is done by washing the surface to be welded with molten cast iron until the former is soft; the fresh metal is then cast and the new neck finished off by turning. Particulars are given of rolls varying from 17 to 30 in. dia. weighing 2 to 4 tons which have been successfully repaired. Metallographic studies show the welded sections to be structurally sound.—M. D. J. B.

**Welding of High-Alloy Castings.** R. D. Thomas, jun. (*Welding J.*, 1952, **31**, Jan., 27s–32s). Cracks in welds in 1-in. thick austenitic heat-resisting steel (15% Cr and 35% Ni) castings have been encountered in each of 24 test plates welded by four foundries using a variety of techniques and electrodes. The groove design of the cast plate is considered very satisfactory as a means of evaluating the welding variables in a test programme, or a means of judging welding procedures and assessing weldability. Tensile tests on a few transverse-weld specimens gave ultimate strengths of 40,000 to 45,000 lb./sq. in. at 1400° F. and 17,000 to 21,000 lb./sq. in. at 1800° F., with fractures occurring sometimes in the weld, sometimes in the base metal.—U. E.

**Stainless Steel Weld Deposits on Mild and Alloy Steels.** H. Thielsch. (*Welding J.*, 1952, **31**, Jan., 37s–64s). This is a detailed review of published and unpublished data on joints between dissimilar metals, made with stainless-steel electrodes. Metallurgical properties of base and weld metals, effects of heat-treatments, and corrosion are discussed. Applications of these joints are outlined. (114 references).—U. E.

**Industrial Brazing. Heating Methods and Equipment.** E. V. Beatson and H. R. Brooker. (*Welding Metal Fab.*, 1952, **20**, Jan., 2–11; Feb., 54–61; Mar., 103–109). Heating methods and details of equipment are discussed and illustrated. The difference between the belt-conveyor and the roller-hearth furnace for brazing in the furnace is discussed. Protective or reducing atmospheres are derived either from anhydrous ammonia, dissociated into its constituent elements, or from coal gas or other fuel gases burnt with a controlled proportion of air with or without the aid of external heat. A brief review is given of the differences between the three types of induction heater, *i.e.*, motor generator, spark-gap converter, and valve generator. An important characteristic of resistance heating is that the heat can be localized round the joint area. Two different types of resistance heating can be used. In one type the electrodes are of carbon, which has a relatively high electrical resistivity, and in the second, called direct-resistance heating, the electrode material is of much lower resistivity. In salt-bath brazing, the work, with brazing materials in place, is put in a molten salt bath and heated to brazing temperature. In the dip-brazing process the parts to be joined are first assembled with predetermined joint gaps and then immersed in molten brazing alloy held in a suitable bath. This method is usually applied to the brazing of aluminium and high-chromium steels.—U. E.

**How to Braze-Weld Cast Iron.** H. D. Drummond. (*Welding J.*, 1952, **31**, Feb., 148–151). The repair of cast iron by bronze welding is described with illustrations—U. E.

**Hints for Silver-Brazing of Stainless Steel.** J. P. Emmerich. (*Welding J.*, 1952, **31**, Jan., 50–53). Particulars are given of some silver–copper–zinc–cadmium alloys for brazing light stainless-steel tanks and cans for processing food. The technique is described.—R. A. R.

**Stainless Brazed Without Fluxing.**—F. W. Beall. (*Steel*, 1952, **130**, Jan. 14, 57). By first plating a thin coating of iron on stainless steel many of the difficulties of furnace brazing without fluxing have been overcome. A thickness of 0·2 to 0·3 mils is used on 18/8 stainless steel when copper brazing at 2150° F. in a DX protective gas atmosphere. Before plating, the material must be activated in an anodizing bath followed by a short cathodizing cycle.—A. M. F.

**A Comparison of Heating Methods for Brazing.** L. F. Spencer. (*Steel Processing*, 1951, **37**, Dec., 617–623; **38**, Jan., 29–34). The compositions and basic requirements of commercial brazing alloys are first discussed. The rest of the article deals in detail with the following brazing methods: Box-type, mesh-belt conveyor, and roller-hearth conveyor furnace brazing; salt-bath brazing; torch brazing; and methods employing induction and resistance heating. The advantages and disadvantages of each method are listed.

**Soldering with a Phosphorus–Copper instead of a Silver Solder.** Z. M. Ryzhik. (*Avtog. Delo*, 1948, No. 9, 30). [In Russian].

**Thickness of Coating of UONI-13 Electrodes.** D. M. Levykin. (*Avtog. Delo*, 1948, No. 9, 28). [In Russian]. The effect of the thickness of the core and coating of a welding electrode on the mechanical properties, chemical composition,

and structure of the deposited metal was determined.—S. K.

**Flame Cutting Solves Armor-Beveling Problems.** R. Sibley. (*Iron Age*, 1951, **168,** Nov. 15, 117–119). Acetogen, a chemically compounded hydrocarbon gas, when properly combined with oxygen, produces an ideal flame-cutting temperature between that of oxy-acetylene and propane. Armour plate can be cleanly cut leaving it ready for welding without further finishing. Speeds are average and a newly designed torch nozzle is all the new equipment required. Bevel-edge angles as low as 20° can easily be cut.—A. M. F.

**Research with a View to Improving the Economics of Oxygen Cutting.** M. Renaudie. (*Rev. Soudure*, 1952, **8,** 40–44). The author examines the factors influencing flame cutting costs and refers to work carried out by British, Belgian, Swedish, and Dutch authorities. Nozzle shapes and oxygen pressures are discussed. The greatest economies can be obtained by concentrating on the design of burners.—M. D. J. B.

**Cutting with Ultra-High Purity Oxygen.** E. H. Roper and J. F. Kiernan. (*Amer. Found. Soc. Preprint*, 1952, No. 57). The authors have found that there is a straight-line relation between the oxygen purity and the cutting efficiency. For purities between 99·0 and 99·83% there is a 2% increase in cutting speed for each 0·1% increase of purity. As between rolled and cast material there was no significant difference, except as regards the difficulty of measurement. The use of oxygen of nearly 100% purity is not a commercial proposition at present.—E. T. L.

## MACHINING AND MACHINABILITY

**How Structure Influences the Machinability of Thin Gray Iron Castings.** E. A. Loria. (*Mat. Methods*, 1952, **35,** Feb., 99, 100). Machinability tests are described, the results of which show that inoculating iron with silicon carbide improves the surface machinability of thin sections.—P. M. C.

**Cutting Temperatures and Metal-Cutting Phenomena.** B. T. Chao and K. J. Trigger. (*Trans. Amer. Soc. Mech. Eng.*, 1951, **73,** Aug., 777–793). The authors consider some important conclusions from an investigation on the mechanism of heat generation during metal-cutting operations. Many changes during the cutting of metals are due to the change in tool-chip interface temperature through its influence on tool-chip friction. The cutting forces and cutting temperatures observed during conventional turning and orthogonal cutting under otherwise identical conditions are considered. The higher heat-dissipating capacity of the tool in orthogonal cutting operations is responsible for the observed differences.

**Basic Factors in Hot-Machining of Merchant Metals.** E. J. Krabacher and M. E. Merchant. (*Trans. Amer. Soc. Mech. Eng.*, 1951, **73,** Aug., 761–776). Studies on the mechanics of cutting at elevated temperatures were made; in these chip friction, shear strength, and machining constant were measured. In addition, tool-chip interface temperatures were calculated. These data were correlated with data obtained from milling tool life tests on the same materials. There are two opposing factors affecting tool life in hot machining. These are the increased ease with which the heat-softened tool material can be abraded away, and the decreased ability of the heat-softened chip and workpiece to produce such abrasion. These two factors can be approximately evaluated from tool temperature data taken in combination with data on the mechanics of cutting.—D. H.

**Surface Temperatures in Grinding.** J. O. Outwater and W. C. Shaw. (*Trans. Amer. Soc. Mech. Eng.*, 1951, **74,** Jan., 73–86). Heat-transfer theory involving a moving heat source is applied to the grinding process to obtain an equation for the mean surface temperature in grinding. This equation predicts surface temperatures as high as 3000° F. for a representative fine grinding operation. The analysis shows that, in finish-grinding, the surface temperature is reduced by decreasing the chip depth of cut.—D. H.

**The Size Effect in Metal Cutting.** W. R. Backer, E. R. Marshall, and M. C. Shaw. (*Trans. Amer. Soc. Mech. Eng.*, 1952, 74, Jan., 61–72). A cutting process involving the formation of very small chips at high cutting speeds (micro-milling) is investigated and the results are applied to a study of the grinding operation. The shear energy involved in grinding is compared with that in turning, micromilling, and the tensile test, and a significant increase in shear energy is observed with decrease in chip size. The shear stress involved in grinding metals under mild conditions is found to correspond to the theoretical strength, which is about $1{\cdot}8 \times 10^6$ lb./sq. in. for steel. The grit depth of cut is shown to be a more important variable in the interpretation of grinding data than the more conventional wheel depth of cut.—D. H.

**Method of Machining Carbide Die for Odd-Shaped Powder Part Illustrates New Way of Cutting Hard Materials.** J. S. Roller. (*Precision Met. Mold.*, 1952, **10,** Mar., 47–50). The paper gives a brief description of a new electro-mechanical system of metal removal termed 'Method X.' Electricity applied through specially shaped electrodes at high current densities results in the physical separation of metal particles from the workpiece. As the electrode is steadily advanced into the work, the metal particles are flushed away by a dielectric bath in which the work is submerged. A cavity following closely the shape of the electrode is thus produced.

**Methods of Investigating the Machining Properties of Metals.** L. Czaplicki. (*Rev. Univ. Min.*, 1952, Series 9, **8,** Feb., 33–43; Mar., 76–88). After a brief illustrated description of three types of metal cuttings (chips and turnings) a mathematical analysis of the theory of cutting is presented. Six methods of investigation are given in detail. These are the measurement of: (1) Force required for cutting; (2) microhardness; (3) ability to be cold worked; (4) life of the cutting tool; (5) effect of temperature on cutting; and (6) heat generated by cutting.

## CLEANING AND PICKLING

**Disposal of Spent Pickle Liquor.** G. Rossi-Landi. (*Mét. et Constr. Méc.*, 1952, **84,** Feb., 120–121; Mar., 183–185). The urgency of the problem of dealing with residual liquids and the effects of ferrous salts on fish are stated. German methods of dealing with river pollution are briefly mentioned. The advantages of three systems of disposal (intermediary reservoirs, dilution, and neutralization) are compared.—R. S.

**Symposium on Liquid Industrial Wastes: Steel Industry.** R. D. Hoak. (*Indust. Eng. Chem.*, 1952, **44,** Mar., 513–520). The author reviews current waste-treatment practice in the steel industry, with special emphasis on spent pickle liquor. Other waste products discussed are slag, blast-furnace dust, and coal chemicals from coke ovens.—C. J. B. F.

**Symposium on Liquid Industrial Wastes: Sulphuric Acid Recovery from Waste Liquors.** F. J. Bartholomew. (*Indust. Eng. Chem.*, 1952, **44,** Mar., 541–545). A practical method is described for recovering the sulphuric acid from the iron-sulphate/sulphuric-acid solutions which go to waste from steel mills and titanium pigment plants. This is done by concentrating the free acid, removing the iron sulphate by salting out, and then decomposing the sulphate for the recovery of the acid value it carries. Also described is a new method of supplying heat to concentrate the liquor, which improves fuel efficiency.—C. J. B. F.

**Pigment Grade Iron Oxides—Recovery from Iron-Containing Waste Liquors.** C. C. DeWitt, M. D. Livingood, and K. G. Miller. (*Indust. Eng. Chem.*, 1952, **44,** Mar., 673–678). A description is given of a continuous pilot plant for the wet process chemical production of synthetic pigment grade iron oxides. The plant has been in production for some time, producing principally red and yellow oxides. The raw materials for these operations were those occurring in commercially used pickling operations. The plant is very compact and simple in construction. The economics of the processes are also discussed.—C. J. B. F.

**Effect of CaO: MgO Ratio in the Neutralization of Pickle Liquor.** F. J. Clauss and L. E. Brownell. (*Iron Steel Eng.*, 1952, **29,** Mar., 63–70). The relationships between the volume of filter cake and the filtration rates obtainable with the two variables lime composition and operating pressure drop of filtration are determined and presented in graphical form. There is an optimum CaO: MgO ratio of approximately 96: 4 parts by weight for obtaining maximum rates of filtration in the practical range of operating pressures. Detailed consideration is given to: Equipment and procedure; rate of the neutralization reaction; volume of filter cake produced; rate of filtration; cake resistivity; use of filtrate for slaking; and finally to the qualities of commercial lime.—M. D. J. B.

**Contribution to the Study of Economies in Pickling.** G. Batta, L. Scheepers, and L. Gendarme. (*Chim. et Ind.*, 1952, **67,** Apr., 577–583). A method of evaluating the effect of inhibitors, and the effect of wetting agents added to the pickling liquor are described. Work on the control of the completion of pickling using an electrochemical method is outlined.—T. E. D.

**From Pickle Plant to Inspection.** J. Eccleston. (Inst. Vitreous

Enamellers: *Foundry Trade J.*, 1952, **82**, May 1, 473–475, 482). The author considers the chemistry of pickling, drying, cover-coat enamelling, titanium opacification, mottling, and enamel sieving.—E. T. L.

**Induction Descaling Proves a Fast Economical Method for Cleaning Steel.** H. Kinaid. (*Mat. Methods*, 1952, **35**, Jan., 97). Details are given of a process developed by the International Harvester Co., and the Tocco Div., Ohio Crankshaft Co., U.S.A. Induction heat is used to raise the temperature of the surface scale rapidly enough for the expansion to make it crack off the cooler base metal. The method is being used successfully to descale hot-rolled bars approximately 3 in. in dia., 10,000 cycles/sec. and 350° F. being the applied frequency and the skin temperature attained.—P. M. C.

**Speeding up the Deburring of Stampings.** W. C. Cowley. (*Steel Processing*, 1952, **38**, Feb., 71, 101). A brief description of the use of Roto-Finish barrelling equipment, for the removal of grinding burrs from clutch discs is given. Thirty-eight discs are treated in a batch, the barrel being rotated at 24 r.p.m. for 20 min. and containing 700 lb. of No. 5B granite chips, 17 lb. of No. 10 Roto-Finish compound, and water.

**A Method for the Investigation of Electropolishing Problems.** K. F. Lorking. (Australian Inst. Metals: *Australasian Eng.*, 1952, Feb. 7, 58–61). A 'Hull' type cell, in which the electrodes are inclined at 35° so that the current density varies across the cell, was used to determine the optimum bath composition for copper in phosphoric acid solutions. The mechanism of electropolishing is also discussed.—P. M. C.

**Degreasing in the Plating Shop.** W. F. Jesson. (*Electroplating*, 1952, **5**, Mar., 77–84). The procedures, in use at the Ionic Plating Co., Ltd., Birmingham, for economizing in the consumption of trichlorethylene are described.—J. P.

**Evaluating Metal Cleaning Efficiency.** S. Spring. (*Metal Finishing*, 1952, **50**, Feb., 65–68). It is suggested that the water-spray pattern is a useful laboratory procedure for determining the proportion of a surface covered with soil; it is also adaptable to plant usage. Several recommendations are made and a list of precautions is given for rendering the method more precise and convenient.—J. P.

**Vapour Blast Liquid Honing.** D. Grant. (*Electroplating*, 1951, **4**, Dec., 377, 378, 384). The use of a suspension of abrasive particles in a liquid, driven by compressed air against a metal surface, for cleaning before plating and painting, and for deburring, is described.—J. P.

**Installation for Sand-Blasting Large Parts.** (*Machinery*, 1952, **80**, Jan. 3, 28–29). The article describes an arrangement whereby the operator can travel round large workpieces in an air-conditioned cab employed in a Pangborn hydro-sand blast room at Falk Corp., Milwaukee, Wis., U.S.A.—E. C. S.

**Flame Cleaning Steel Structures.** Commonwealth Industrial Gases, Ltd. (*Commonwealth Eng.*, 1952, **39**, Jan. 1, 225–228). Furnace scale consisting largely of burnt sand, metallic oxide, and mill-scale formed on rolled steel sections and plates can be readily removed by the oxy-acetylene flame. The specification for flame-cleaning structural steel, as issued by the American Institute of Steel Construction, is given. Flame-cleaning is an ideal means of preparing a steel surface for painting. The equipment, labour force, and procedure employed by the New South Wales Department of Railways is briefly described.—J. P. S.

**The Chemical Polishing of Iron and Mild Steel.** L. Beaujard. (*Compt. Rend.*, 1952, **234**, Jan. 21, 440–442). A reagent consisting of hydrofluoric acid 70 parts, nitric acid 30 parts and water, 300 parts, at a temperature of 60° C., gives the best results. The addition of chemicals with an OH group slows the rate of attack without affecting the quality of polishing.—A. G.

**Electrolytic Polishing.** (*Automobile Eng.*, 1952, **17**, Feb., 56). The advantages of electropolishing stainless steels and irons are very briefly discussed.—P. M. C.

**Felt for Finishing—Metalworking Applications Expand.** L. D. Gruberg. (*Steel*, 1952, **130**, Feb. 4, 88–89, 110). Felt in a wide range of thicknesses and densities is being used extensively for precision grinding, polishing, and buffing. Deep-drawing dies, combustion chambers, and darning needles are some of the wide variety of products given a final surface finish by felt bobs or wheels. Successful use of belt wheels depends upon selection of belts of uniform texture and suitable density, fabricated from good-quality wool.—A. M. F.

**More Scrap, More Tin—Detinning Produces Both.** (*Steel*, 1952, **130**, Jan. 28, 70–72). An integrated detinning plant at the Weirton Steel Co. is described. The annual capacity is 300,000 lb. of pig tin and 30,000 tons of bundled scrap. Baled side trimmings are sawn open before being placed in drums for the detinning operation which is carried out with a 50% solution of sodium hydroxide with additions of sodium nitrate. Scrap is then rebundled for the open-hearth plant. The sodium stannate solution is converted to tin oxide and reduced to tin in electric furnaces.—A. M. F.

**The Commercial Electropolishing of Stainless Steels.** P. A. Charlesworth. (*J. Electrodep. Tech. Soc.*, 1950, **26**, 43–53). The economics and conditions for the commercial electropolishing of stainless steels are discussed and enumerated. A solution developed (Brit. Pat. 622,118) satisfying these requirements, contained sulphuric acid 55, phosphoric acid 22, water 23, additive (*e.g.*, aniline) 2 parts by weight. The operating conditions for 18/8 and 12/12 stainless steels were: C.d. 0·5 to 1·5 amp./sq. in.; bath temperature, 55° C.; voltage at source, 6 to 9 V.; time of treatment, 5 to 30 min.—R. L. B.

**Cleaning and Preparation of Metals for Electroplating. IV. Degreasing Evaluation Tests: Sequential Testing.** H. B. Linford and E. B. Saubestre. (*Plating*, 1952, **39**, Jan., 55–63). This report contains appendices dealing with variance analysis, statistical analysis of results obtained in previous parts of this paper, sensitivity data, and laboratory results.—J. P.

**Machine of the Liné-Gorcy Type for the Removal of Scale from Steel Wire.** P. Ewald. (*Draht*, 1951, **2**, 6, 175–176). The operation of the above machine for mechanically descaling steel wire rod and drawn wire is described.—V. G.

**Methods of De-enamelling Vitreous-Enamelled Components.** W. H. Billingham. (Inst. Vitreous Enamellers: *Sheet Metal Ind.*, 1952, **29**, Mar., 269–272).

**Induction Heat Cuts Descaling Costs.** (*Iron Age*, 1952, **169**, Jan. 17, 106). Removal of scale on round bar stock by induction heating has been successfully tried at the Farmall works of International Harvester. The temperature of the surface scale is raised rapidly enough to cause it to separate from the base metal. This, together with the progressive heating and irregular electrical characteristics, breaks the scale into small pieces.—A. M. F.

## PROTECTIVE COATINGS

**Periodic Reverse Current Plating Processes.** A. Dias Santilhano. (*Metalen*, 1952, **7**, Mar. 28, 99–106). [In Dutch]. In the struggle to reduce costs and improve quality and output, bright pickling baths have played a major part for a number of years. Periodic reverse current plating is described and its advantages enumerated.—R. S.

**Heating Systems for Plating Vats.** (*Product Finishing*, 1952, **5**, Feb., 48–56). The advantages and disadvantages of various types of heating system for plating and cleaning vats are discussed.—J. P.

**Cathode Sputtering.** (*Product Finishing*, 1952, **5**, Feb., 66–68). The principles of, and equipment used for, cathode sputtering of metals on to metallic and non-metallic surfaces are described.—J. P.

**The Vacuum Coating of Metal Articles.** L. Holland. (*Metal Ind.*, 1952, **80**, May 2, 351–354). The metallizing of metal articles by vacuum evaporation on to a lacquered substrate avoids expensive base polishing. The author discusses the properties required of lacquer coatings used in combination with evaporated films, the influence of the surface finish of the base on the quality of the evaporated coating, the vacuum-coating properties of several commercial lacquers, and the tinting of evaporated aluminium films by dyeing the lacquer protective coating.—P. M. C.

**Surface Treatment and Plating in Naval Aircraft.** G. S. Mustin. (*Metal Finishing*, 1952, **50**, Feb., 53–61, 73). The types of electrodeposited coatings and surface treatments employed on U.S. naval aircraft are described and the reasons for the present specifications requirements are reviewed. These specifications have led to less trouble in the operation of naval aircraft.—J. P.

**An Introduction to Clad Metals.** W. L. Keene. (*Iron Steel Eng.*, 1952, **29**, Mar., 109–117). After considering the general principles involved in cladding, the author examines the characteristics of clad metals, the principles of bonding, and the various methods of cladding, including pressing, casting, rolling, and sintering methods. Reference is made to some 150 workers in this field and to some 300 patents granted.

**A New Anodising Plant.** (*Product Finishing*, 1952, **5**, Mar., 70–77). The equipment used by Scrib, Ltd., Brimsdown, for

polishing, cleaning, anodizing, and dyeing ball-pen caps is described and illustrated.—J. P.

**Chromium Plating with the Bornhauser Chrome Solution.** F. Taylor. (*Electroplating*, 1952, **5**, Apr., 109–113). The Bornhauser chromium plating solution contains sodium tetrachromate as a principal constituent and works at room temperature and at a wide range of current densities (200–900 amp./sq. ft.). Its cathode efficiency is high (about 30%) but the deposit is grey and requires buffing. Its use has so far been mainly confined to the direct plating of zinc base die castings. The methods of operation and applications of the process are given, together with details of the composition and maintenance of the solution.—J. P.

**Some Experience with a Proprietary Red Bronze Plating Solution as a Substitute for Nickel.** F. S. Duc. (*Electroplating*, 1952, **5**, Apr., 123). The precautions to be observed in controlling a proprietary cyanide bronze plating solution and in preparing the deposit for receiving chromium are described. The corrosion resistance of the bronze–chrome deposit is good.—J. P.

**Modified Bronze Plating as a Substitute for Nickel.** G. Schmerling. (*Electroplating*, 1952, **5**, Apr., 115–118). The properties of a copper–tin alloy electrodeposited from a patented cyanide-type bath are described. It appears to have protective properties of the same order as those of nickel; it is easy to polish to a high finish and is very suitable as an undercoat for bright chromium. Existing nickel-plating equipment may be used under average conditions and with the average personnel. The materials required are neither scarce nor expensive and the process is no more costly than nickel plating.—J. P.

**The Tinplate Problem in Spain.** E. Diaz Varela Ceano-Vivas. (*Inst. Hierro y Acero*, 1952, **5**, Feb., *Special Issue*, 159–173). [In Spanish]. A critical survey is made of packet rolling and continuous and semi-continuous sheet rolling. Batch tinning and the continuous electrolytic process are compared.—R. S.

**Hot-Dip Tinning.** W. E. Hoare. (*Product Finishing*, 1951, **4**, Oct., 70–82, 99). The procedures employed for the hot-dip tinning of steel and copper in the form of wire, sheet, strip, and fabricated articles are described.—J. P.

**Development and Production of Electrolytically Tinned Steel Sheet.** (*Hutník* (Prague), 1952, **2**, Apr., 90–92). [In Czech]. This is a survey of methods and the principles involved in electrolytic tinning practice.—P. F.

## POWDER METALLURGY

**The Nature and the Production of the Hard Metals.** R. Mitsche. (*Berg- hüttenmänn. Monatsh.*, 1941, **89**, Sept., 105). Hard metals with a Rockwell hardness of 75–90 are discussed. These are generally double carbides with very high melting points. By themselves they are very brittle, which limits their use. Cobalt is used as a binding metal, which increases their toughness.—R. J. W.

**New Methods in the Production of Hard Metals.** R. Mitsche. (*Berg- hüttenmänn. Monatsh.*, 1939, **87**, Oct., 185–189). Tungsten carbide with 6% cobalt as binder has a conductivity three times greater than that of high-speed steels, hence it is extremely useful for cutting tools. The two methods of manufacture of carbides, by (*a*) melting at temperatures of about 2000° C. and subsequent separation of the carbide from the melt, and (*b*) the sintering process, are described.—R. J. W.

**The Bonding of Sintered to Compact Metals.** W. Hofmann and E. Schmalenbach. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 135–143). The possibility has been studied of forming a bond between sintered iron and solid steel by pressing and sintering the powdered metal against a steel backing, as an alternative to the conventional soldering or brazing methods. The influence of grain size, pressing load, and sintering time and temperature on the adhesion were determined. Because of the unavoidable porosity at the junction, the adhesion was comparatively low. It could be markedly increased by sintering in the presence of a liquid, in this case copper, when the mechanical filling of the pores and the alloying between the copper and iron exerted a favourable effect. The possibility of forming a bond by hot-pressing is discussed.

**Powder Metallurgy.** (*Chem. Age*, 1952, **66**, Mar. 7, 345–347). Powder-metallurgy literature is reviewed; scientific and theoretical as well as technical and economic publications are covered, and the results of some recent Russian work are indicated.—T. E. D.

**Powder Metallurgy 1925–1950–19??.** A. J. Langhammer. (*Metal Progress*, 1952, **61**, Jan., 72–75). The history of powder metallurgy is reviewed. Techniques and manufacturing equipment have been improved so that plain or barrel-type self-lubricating bronze bearings are now available. Finished machine parts have made it possible to eliminate more than 20 machine-tool operations on some items.—J. P. S.

**Powder Metallurgy's Contribution to High-Temperature Materials.** H. W. Greenwood. (*Metal Treatment and Drop Forg.*, 1952, **19**, Feb., 75–80). This is a very general review of the development of powdered metals and their application during recent years to high-temperature problems.—P. M. C.

**Trends in Powder Metallurgy.** H. W. Greenwood. (*Metallurgia*, 1951, **44**, Dec., 291–294). The development of sintered metal products in the post-war years is reviewed. Surface coatings on the original powders can modify the physical properties of the sintered product and give an enhanced resistance to corrosion. The manufacture of porous bearings, jet-engine compressor blades, and gears by infiltration and impregnation processes is discussed. The future application of powder-metallurgical principles to the manufacture of high-temperature alloys is also considered.—B. G. B.

**Trapping of Gases in Cold-Compacted Powders.** J. Williams. (*J. Iron Steel Inst.*, 1952, **172**, Sept. 19–24. [This issue].

**Experimental Study on the Kinetics of Sintering Metal Powder at Constant Temperature. I.** T. Okamura, Y. Masuda, and S. Kikuta. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1949, **1**, Dec., 357–363). [In English]. Isothermal changes of the breaking strength and shrinkage of sintered copper and iron were measured at various temperatures. Thence empirical formulae for the sintering rate were derived in terms of time, temperature, and porosity.—J. G. W.

**On the Method of Mechanically Pulverizing Metal by Cutter Mill.** T. Okamura and K. Inagaki. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1950, **2**, Oct., 809–821). [In English]. Lead, cadmium, tin, silver, copper, iron, cast steel, and an imitation gold–copper alloy were pulverized in an experimental mill by a shearing action. The study covered mill performance, relation between time and work done, effect of metal properties, size, particle distribution, and shape of powder produced. The action of the mill is explained.—J. G. W.

**The Manufacture of Cemented Tungsten Carbide Dies.** B. E. Berry. (*Wire Ind.*, 1952, **19**, Jan., 45–55). A brief survey is made of the landmarks in the history of tungsten carbide. Preparation of the raw materials from ores is described in detail, stress being laid on the influence of variations in intermediate operations on the final product.—J. G. W.

**The Evaluation of Screen Analysis in Powder Metallurgy.** A. Vambersky. (*Hutnické Listy*, 1951, **6**, July, 320–322). [In Czech]. The distribution of grain sizes in metallic powders prepared by means other than mechanical crushing should follow the normal distribution law. It is suggested that for size analysis a (log frequency)/(log mean grain weight) co-ordinate system be used on which the Gaussian distribution appears as a straight line. Any deviations from a straight line may show the manner in which a powder was prepared, *i.e.*, from several components, or whether it was prepared by mechanical grinding. In the latter case the distribution curve obeys the Rossin-Rammler-Bennett law. An example of the statistical quality control of iron powder is explained.

**The Properties of Cemented Carbide Alloys Presented for Comparison.** C. Ballhausen. (*Stahl u. Eisen*, 1952, **72**, Apr. 24, 489–492). The properties of WC/TiC/Co alloys are presented on a series of three-dimensional rectangular diagrams. In each case the base rectangle has the volume ratio of WC to TiC and the cobalt content as ordinates. The vertical axis shows compression strength, elastic modulus, hardness, relative bend strength, thermal expansion, and cutting properties. Some suggestions are made for standardizing the nomenclature of these alloys.—J. P.

**A Study of the Properties of Sintered Steels.** V. Chiaverini and C. de Revoredo Barros. (*Bol. Assoc. Brasil. Metais*, 1951, **7**, July, 346–365). [In Portuguese]. A preliminary study is made of the sintering of iron powders from various Brazilian ores. Full details of mechanical and physical properties are given. There was practically no difference in the quality of sintered products using sponge-iron powders with or without final hydrogen reduction. Differences in hardness and strength depend on carbon content and moulding pressures.

**Powder Metal Locking Part Is Bent 4 deg. and Assembled**

**Under Stress to Gain Spring Action.** A. L. Fabens. (*Precision Met. Mold.*, 1951, **9**, Dec., 29–31). The advantages of the production of a lock for the firing pin on the 0·38 calibre Ramset tool by powder metallurgy are discussed. The part is produced by the Metal Powder Products Co., Dayton, Ohio.—D. H.

**Mechanical Precision of Parts Obtained by the Powder Metallurgy Process.** R. Girschig. (*Microtecnic*, 1951, **5**, Nov.–Dec., 345–350). The application of the powder-metallurgy process to the manufacture of mechanical parts made of bronze, brass, or iron is discussed. A simple self-lubricating cylindrical ring from porous bronze is given as an example.—H. D. W.

**Stainless Steel Filter with High Strength Produced by Powder Metallurgy.** (*Precision Met. Mold.*, 1951, **9**, Nov., 39). Brief details are given of an explosion-proof screen of the 'Staticator,' a unit which detects the presence of static electricity in places where there is an explosion hazard. The screen is made of almost spherical stainless-steel particles, sintered to give a highly porous structure with high strength.—D. H.

## PROPERTIES AND TESTS

**On the Influence of Mechanical and Heat Treatment on the Behaviour of Steel up to the Elastic Limit.** W. Köster. (*Inst. Hierro y Acero*, 1952, **5**, Jan.–Mar. 221–240). [In Spanish]. The author considers the influence of grain size, tempering temperature, ageing subsequent to drawing, and speed of testing on the elastic limit. The effect of heat-treatment below the $A_1$ point, and of precipitation hardening on the yield point are examined. The solution and precipitation of carbon in the ferrite affects the plastic behaviour whilst the homogeneous precipitation and the redissolution into the crystal network affects the elastic behaviour. Precision measurements of small elongations show that permanent set takes place below the elastic limit. The beginning of elongation is retarded.—R. S.

**Effect of Specimen Length on the Strength of a Material with Random Flaws.** K. E. Puttick and M. W. Thring. (*J. Iron Steel Inst.*, 1952, **172**, Sept., 56–61). [This issue].

**The General Torsional Relaxation Properties of a Bolting Steel.** D. N. Frey. (*Trans. Amer. Soc. Mech. Eng.*, 1951, **73**, Aug., 755–760). An investigation of the tensile relaxation properties of a Cr–Mo–Si–V commercial high-temperature bolt steel at 1000° F., by means of the step-down relaxation test, is reported.—D. H.

**Improving the Mechanical Properties of Low-Alloy Heat-Treatable Steels by Adjusting Heat-Treating Temperatures and Times.** W. Eilender, H. Arend, and W. Neuhaus. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 67–72). Investigations have been carried out on several low-alloy heat-treatable steels to determine whether their impact and tensile strengths could be improved by modifying the usual heat-treatment. The goal of the tests was to obtain, before quenching, a homogeneous austenite as free as possible from nuclei, since only in this way can a uniform transformation to martensite be ensured. It would also be possible, by such a procedure, to change over from oil to water hardening without fear of cracking and distortion. By suitably raising the normal annealing temperature, lowering the hardening temperature and varying the hardening time, it was possible to achieve a general increase in impact and tensile strengths and an improvement in depth of hardening and resistance to temper brittleness. The experimental results have been confirmed in work's trials on drop forgings.—J. P.

**Ductile and Brittle Fracture.—III.** R. Calvo Rodes. (*Inst. Hierro y Acero*, 1952, **5**, Jan.–Mar., 314–326). [In Spanish]. In this part the author considers the micromechanism of rupture in alloys in relation to impurities.—R. S.

**Security Against Brittle Fracture in Structural Steels for Welding.** A. Fry. (*Inst. Hierro y Acero*, 1952, **5**, *Special Issue*, Jan., 1–22). [In Spanish]. The nature of brittle fractures is described. Theoretical principles of the strength of materials are stated followed by an exposition of the metallurgical principles pertaining to the problem of brittle fracture. The fundamental processes which constitute ageing are considered. Brittle fracture is not only influenced by the multi-axiality of the state of stress, but also by the capacity of the steel for internal deformation. Special attention is paid to the testing of weldable steels for brittle fracture. Data on the Schnadt notch impact tests on basic-Bessemer and open-hearth steels, and the properties and uses of some Austrian structural steels for welding are presented.—R. S.

**Control of Residual Stress in Butt-Welded Steam Piping: An Investigation by Mechanical Relaxation and X-Ray Methods.** C. R. Tottle, A. Cowan, and R. W. Firth. (*Iron Coal Trades Rev.*, 1952, **164**, Feb. 22, 433–440). The authors have investigated the residual stresses in molybdenum and chromium steel butt-welded steam pipes, using mechanical relaxation and X-ray methods. The surface stresses measured by X-ray methods were found to be high in value, showing a sharp peak distribution of circumferential stress around the welded joint. It is concluded that stress relief is necessary in welded pipes to avoid concentration of stress and to minimize plastic flow due to creep at service temperatures.—G. F.

**Properties and Application of Resistance Strain Gauges.** K. Fink and C. Rohrbach. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 75–81). The more important properties of the types of electric resistance strain gauge at present available in Germany (Phillips and Huggenberger) have been investigated and some advice is given on their installation and use. The gauges are suitable for many research problems.—J. P.

**Errors in Stress Determination at the Free Boundaries of "Frozen Stress" Photoelastic Models.** V. M. Hickson. (*Brit. J. Appl. Phys.*, 1952, **3**, June, 176–181). Errors, apart from those due to the use of imperfect material, are listed, and estimated where possible. Particular attention is paid to the case of stress concentration, where small radii introduce errors which would be negligible elsewhere, and minimum surface radii and maximum slice thickness for any given error, are specified.—E. T. L.

**The Influence of Residual Stresses on the Fatigue Resistance of Structures.** M. Ros. (*Rev. Soudure*, 1952, **8**, No. 1, 23–39). The author describes tests on a wide variety of samples submitted to initial stresses before fatigue testing, these stresses being imposed by mechanical action as well as by welding. The author believes that residual stresses have little influence on fatigue resistance, provided there are no discontinuities in the metal structure in the form of hair-line cracks, and the metal is capable of plastic deformation.—M. D. J. B.

**On the Nature of 'Training' in Fatigue Tests.** F. Vitovec. (*Berg- Hüttenmann. Monatsh.*, 1952, **97**, Jan., 3–5). An explanation is advanced of the phenomenon of 'training' observed by E. Siebel and G. Stählı, who showed that the removal of a surface layer by etching or grinding from a specimen which had been subject to 'training' cycles before prolonged fatigue tests resulted in an appreciable increase in fatigue limit. In 140 experiments the etching rate of mild-steel specimens subject to $10^6$ 'training' cycles was determined as a function of the depth below the surface. The rates of etching at the surface, and at a depth of a few hundredths of a millimetre, of specimens previously fatigue-stressed were respectively higher and lower than the rates at corresponding positions on similar specimens not previously stressed. The reduction in rate below the surface is associated with a reduction of the free energy resulting from the healing-up of lattice faults. The healing-up is in turn related to the observed effects of 'training.'—R. A. R.

**Study of Crystalline Distortion Produced in Metals by Alternating Stresses.** P. Laurent. (*Publications Scientifiques et Techniques du Ministère de l'Air*, 1952, No. 256, 1–116). A new fatigue testing machine is described; it is used for studying the effects of alternating stresses, both torsional and bending. A theoretical calculation of the deformation for a given stress is made, and the results of tests on aluminium are given. The effect of both kinds of stress on grain structure is examined. The behaviours of annealed and cold-worked samples are compared.—T. E. D.

**Hardness Meters and Their Use in the Examination of the Heat-Affected Zone in Welds.** H. T. Schaap. (*Lastechn.*, 1952, **18**, Mar., 27–33). [In Dutch]. The advantages and disadvantages associated with Rockwell, Brinell, Vickers, and microhardness instruments are stated and the different scales are correlated.—R. S.

**Scratch-Hardness in C.G.S. Units.** W. Ehrenberg. (*Z. Metallkunde*, 1941, **33**, Jan., 22–23). Scratch-hardness, like indentation hardness, may be expressed in kg./sq. mm. The ratio scratch/indentation hardness for loads of $1\frac{1}{4}$–10 kg. is found for steel to be 1·90 (using a sphere of 8 mm. in dia.) and for iron, 1·00 (using a pyramid of 150° angle or a cone of 120° angle), and 2·10 (using a sphere 8 mm. in dia.).—K. G.

**The Influence of Cold Deformation on the Ageing of Mild Steel.** W. Gruhl. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 39–46). The change of electrical resistance with time after

cold-drawing of annealed and slowly cooled mild-steel wires (0·02% C, 0·005% $N_2$) has been measured. The degree of reduction varied from 8 to 75% and the ageing temperature from 20 to 200° C. The fall in specific resistance during ageing increases with increasing degree of deformation and, for a given deformation, decreases with increasing temperature. Two causes are suggested for the fall: (1) The solubility of carbon and nitrogen in the equilibrium solid solution is depressed by cold work; and (2) as a result of the heat generated during drawing, there is a re-solution of cementite or iron nitride nuclei so that the deformed metal becomes once more capable of precipitation. This permits an interpretation of the processes which bring about a yield point and mechanical ageing. It can be assumed that it is not carbon or nitrogen dissolved in the form of an atmosphere round dislocations that is responsible for these phenomena, but that which is present as precipitated cementite or iron nitride. The yield point occurs when the dislocations free themselves from the precipitated material; it does not occur immediately after plastic deformation, but reappears after ageing because there is then a re-formation of a precipitate on the dislocations. The disappearance of the yield point in quenched and aged steel finds an interpretation in these concepts, but blue brittleness is not thus explained.—J. P.

**Change in Yield Strength During Aging in Iron.** C. A. Wert. (*Trans. Amer. Inst. Min. Met. Eng.; J. Met.*, 1951, **3,** Dec., 1179–1180). The author describes an investigation into the change in yield strength accompanying the ageing of iron, employing measurements of internal friction. It is shown that the peak yield strength increases as the ageing temperature decreases, and that the increase in yield strength occurs simultaneously with the ageing precipitation.—G. F.

**Differences in the State of Ferromagnetic Materials in Weak Magnetic Fields or in the Unmagnetized State.** H. Fahlenbrach. (*Arch. Eisenhüttenwesen*, 1952, **23,** Jan.–Feb., 47–51). An attempt has been made, without success, to prove that the differences between ferromagnetic materials demagnetized by different methods are due to different distributions of domain orientation.—J. P.

**Investigation into the Most Suitable Chemical Composition of Permanent Magnet Steel with Approximately 4% Chromium, 2% Cobalt and 0·5% Tungsten (Co040).** W. Knorr. (*Arch. Eisenhüttenwesen*, 1952, **23,** Jan.–Feb., 53–55). The influence of the contents of carbon (0·9–1·2%), chromium (3·3–4·1%), cobalt (1·6–3·0%), and tungsten (0·4–0·8%), and of the sum of the cobalt and tungsten, or of chromium, cobalt, and tungsten, on the magnetic properties of Co040 steel has been investigated on samples from 41 heats. The cobalt and tungsten contents exert the greatest influence; their effects are additive and a total of 2·8% should be aimed at. The following composition is recommended: 0·95–1·10% C, 0·50–0·70% Si, 0·30–0·50% Mn, 1·9–2·3% Co, 3·75–4·25% Cr, and 0·6–0·8% W.—J. P.

**Magnetic Collapse Processes in Iron and Nickel.** F. Förster and H. Wetzel. (*Z. Metallkunde*, 1941, **33,** Mar., 115–124). The individual Barkhausen jumps by which ferromagnetics are magnetized are recorded oscillographically and the mean size of the magnetic elements determined. In cold-drawn iron wire it increases with increasing temperature of annealing, due to the removal of second-order strain. Further annealing reduces the element size as the annular first-order strain is released. During tension, the element size decreases long before measurable plastic deformation occurs.—K. G.

**Variation with Time of Magnetic Collapse Processes in Metals.** F. Förster and E. Scheil. (*Z. Metallkunde*, 1940, **32,** June, 165–173). The twinning of bismuth, the $\beta \rightleftharpoons \alpha$ transformation of zirconium, and the martensite transformation below room temperature of a 25% Ni–Fe alloy were studied and the changes in resistance measured. During the martensite transformation, there is a rise in resistance, followed by a decrease to less than the original value. This lasts $7 \times 10^{-8}$ sec. and is followed by damped oscillations of 12 kilocycles frequency. These vibrations are influenced by the constitution of the wire. With deformed wires there is an initial minimum in the resistance followed by oscillations of 100 kilocycles frequency. The mechanism of this reaction is discussed at length and compared with the rather slower transformation above room temperature.—K. G.

**Apparatus for the Rapid Determination of Magnetic Quantities.** F. Förster. (*Z. Metallkunde*, 1940, **32,** June, 184–190). An electronic apparatus is described for use with wire specimens, which gives an instantaneous picture on an oscilloscope of the hysteresis loop. Both hard and soft magnetic materials may be tested at up to 900° C. A very sensitive differential method may be used for testing the homogeneity of a coil of wire. Saturation, coercivity, and magnetostriction can be calculated. Examples of applications of the apparatus are described.—K. G.

**Effect of Varying the Rate of Reduction on the Magnetic Properties, Ultimate Tensile Strength, and Resistivity of 18/8 Stainless Steel Wire.** S. Storchheim. (*Trans. Amer. Inst. Min. Met. Eng.; J. Met.*, 1951, **3,** Dec., 1181–1183). In the investigation described, the author shows that increasing the drawing rate of commercial 18/8 stainless steel results in an increase in coercive force and decreases in remanence, tensile strength, and resistivity. The effects of analysis changes are also given, from which the author concludes that an 18/8 stainless steel analysis which might normally be considered inferior for a particular specification, can be utilized by the correct choice of drawing speed.—G. F.

**Magnetic Anisotropy in Rolled Iron–Nickel Alloys.** H.-W. Conradt, O. Dahl, and K. Sixtus. (*Z. Metallkunde*, 1940, **32,** July, 231–238). Cold rolling leads to strong magnetic preference in the direction of rolling, even for the alloy composition where the anisotropy constant vanishes. The rolling anisotropy is eliminated by annealing at temperatures lower than those at which recrystallization commences: thus the total anisotropy is separated into a texture and rolling component. The rolling anisotropy shows a maximum at mean degrees of deformation and at 70% Ni; previous heat-treatment leading to superlattice formation increases it. Parallel to it is a strong anisotropy of the coercivity which decreases at high deformation. The increase in resistance due to deformation shows the same dependence on nickel content and heat-treatment as the rolling anisotropy. Explanation of these observations by current theories is not possible.—K. G.

**Hysteresis Losses in Silicon Steels.** V. S. Giron Nuñez. (*Inst. Hierro y Acero*, 1952, **5,** Jan.–Mar., 298–307). [In Spanish]. Hysteresis loss was determined in four sheets of silicon steel for maximum magnetic induction values of 16,000 gauss. The possibility of applying the Steinmetz formula was considered. Within the range of 1000 to 13,000 gauss the experimental results also satisfy the formula of Richter. For fairly high values of magnetic induction, the results satisfy the lineal relation of Brailsford. A new method of determining the hysteresis loss in silicon steels is described. The loss is determined by measuring the power required to rotate three small strips in a homogeneous magnetic field produced by a Helmholtz system. The results obtained by the present method are compared with those found in the same material by the ballistic method.—R. S.

**Non-Destructive Testing of Materials by Means of Ultrasonic Waves.** J. Krautkrämer. (*Werkstoffe u. Korrusion*, 1952, **3,** Apr., 124–127). Ultrasonic waves are impelled into the part to be tested through an exploring head placed on its surface. If a defect is encountered, the waves are reflected and the echo is taken up by the head and registered on a luminous screen. The author advocates the extension of these methods to the chemical industry and describes how this can be done for plates and sections, castings, tubes, and welds. He has constructed an apparatus for this purpose, which is fitted with a variety of test heads, permitting either normal or oblique impulses of the ultrasonic waves. For testing welds, twin heads are provided. Each acts both as an emitter and as a receiver, so that if the weld is sound only a well-defined control echo is registered. Defects are registered symmetrically on both sides of the control echo and, if serious, result in its suppression. The control echo is a useful check that the apparatus is working properly.—J. C. H.

**Non-Destructive Testing of Materials with the Ultrasonic Echo-Sounding Method.** A. Lutsch. (*Arch. Eisenhüttenwesen*, 1952, **23,** Jan.–Feb., 57–65). The principles and construction of the ultrasonic echo apparatus are described and the use of this method, employing longitudinal and transverse waves, for detecting defects in a variety of materials is reviewed at length. The conditions governing choice of frequency and size of transmitter head, and precautions to be observed during testing are indicated.—J. P.

**Ultrasonic Flaw-Detector.** (*Aircraft Prod.*, 1952, **14,** Apr., 126–129). The principle of operation and recent developments in the echo method of flaw detection are described. The

equipment is illustrated and two examples of presentation on a cathode-ray tube are given. These are the Sonoscope and A-scope methods. Thickness measurements may also be made.—T. E. D.

## METALLOGRAPHY

**Determination of the Resolving Power of Autoradiography as Used on Metallic Specimens.** M. Hillert. (*Research*, 1952, **5**, Apr., 192–194). The method of nuclear reaction radiography was used to determine the resolving power of autoradiography as applied to metals, taking an iron–boron alloy as an example.

**Electron Metallography.** R. D. Heidenreich. (*Bell Lab. Record*, 1952, **30**, Mar., 101–105). A brief description of electron microscopic and diffraction techniques and examples of their application to the study of alloy structures are given.—B. G. B.

**A Method for the Electron and Optical Microscopic Examination of Identical Areas.** E. D. Hyam and J. Nutting. (*Brit. J. Appl. Phys.*, 1952, **3**, June, 173–176). The authors outline the difficulties of using the standard dry-stripping technique for examination of an area by two methods. They describe an attachment to fit over the objective lens of a bench metallurgical microscope, which enables replica supporting grids to be positioned precisely over any point. The mode of operation is dealt with, and applications of the method are indicated.—E. T. L.

**Nuclear Reaction Radiography and Auto-Radiography of Metals.** M. Hillert. (*Metal Treatment and Drop Forg.*, 1952, **19**, Mar., 135–137). Brief comments are made on the new radiographic method of inspection called nuclear reaction radiography. Reference is made to the examination of an Fe–B alloy, but no details of experimental techniques are given. The importance of resolving power in autoradiographic work is stressed, and some controlling factors discussed.

**Useful Etchants for Electron Metallography.** W. L. Grube. (*Trans. Amer. Inst. Min. Met. Eng.*; *J. Met.*, 1951, **3**, Dec., 1171–1173). The author describes and illustrates the use of various etchants on typical specimens in electron metallography. The success of a particular etchant in this field cannot always be predicted from experience in light metallography, but etchants used in the latter method form a useful starting point for the development of suitable electron metallography etchants.—G. F.

**Metallographic Reagents for the Study of the Precipitation of Carbides in 18/8 and 25/20 Cr–Ni Steels.** (*Inst. Hierro y Acero*, 1952, **5**, Feb., *Special Issue*, 180–208). [In Spanish]. The suitability of seven reagents for indicating the precipitation of carbides in two Spanish steels is studied. These included Zeiss No. 4, Homecourt, Curran's, Marble's, chromic acid, Murakami's and, finally, the electrolytic method (using oxalic acid). With the exception of Murakami's reagent, all of them proved to be suitable.—R. S.

**Identification of Certain Silicon Carbides.** W. S. Owen and and B. G. Street. (*J. Iron Steel Inst.*, 1952, **172**, Sept. 15–18). [This issue].

**Mechanism of Fracture of Pearlite.** V. Zedník and Z. Kadeřávek. (*Hutnické Listy*, 1951, **6**, May, 211–220). [In Czech]. Fracture mechanisms in pearlite subjected to impact have been studied fractographically on notched samples of eutectoid carbon steel in the temperature range of − 195 to + 150°. In the first stage of fracture, cracks arise selectively at the boundaries of the ferrite–cementite lamellæ in a number of grains having lamellæ favourably orientated with respect to the tensile stresses acting on them. It appears that the start of a fracture is conditioned by the strength of the boundary cohesion between the two phases. The stress concentrations in the numerous microcracks so formed facilitate the progress of the second stage in which these cracks extend and coalesce, and which proceeds preferentially across the grains and in directions other than parallel to the lamellæ. Crystallographic defects and grain size have observable effects on the character of the spread of fractures. Practical uses of fractography are reviewed.—P. F.

**Grain Refinement in Steels after Hot Working.** R. Werner. (*Berg- Hüttenmänn. Monatsh.*, 1952, **97**, Jan., 15–17). The author examines the effect of various heat-treatments and methods of deformation on the grain structure of steels.—P. F.

**Influence of Thermal and Mechanical Treatments Before Critical Working on the Recrystallization of Iron.** M. Mouflard and P. Lacombe. (*Rev. Mét.*, 1952, **49**, Feb., 140–144). The existence of Lüders lines is related to the appearance of a step in the tensile curve, the size of which is a function of composition and of previous treatment. By systematically reducing the Piobert Lüders phenomena, a value for the critical working much lower than previously recognized has been attained.—A. G.

**Formulation of a Theory of Recrystallization.** U. Dehlinger. (*Z. Metallkunde*, 1941, **33**, Jan., 16–20). In cold-worked, polycrystalline metals, two modes of lattice deformation (which can be studied by suitable single-crystal experiments and which possess quite different limits of stability) occur: Dislocations, which are resolved by jumps of single atoms, and bending of whole lattice regions. During recovery, the dislocations are eliminated, while the nucleation for recrystallization depends on the second type of deformation. This is considered from the atomic standpoint : the differences in density of different parts of the bent lattice require a form of chain reaction for their removal. The nuclei obtained in this manner contain little distortion energy and their growth is similar to that in crystallizing melts.—K. G.

**Form of the Cooling Curve.** G. Masing. (*Z. Metallkunde*, 1941, **33**, Jan., 36–37). Analytical derivations are given for the shape of the cooling curves of mechanical mixtures and mixed crystals. The expressions obtained are in complete agreement with, and extend the equations of, Hanemann.

**Observations on Rapidly Quenched Iron–Carbon Melts.** G. Falkenhagen and W. Hofmann. (*Arch. Eisenhüttenwesen*, 1952, **23**, Jan.–Feb., 73–74). Iron–carbon melts containing up to 2·5% carbon have been quenched extremely rapidly by drawing the metal into a water-cooled mould by suction. Back-reflection X-ray photographs have shown the presence of austenite in samples with carbon contents corresponding to those of the melts. Above 1·6% carbon, a small proportion of cementite was also found in the fine structure. The austenite formed from the melt occasionally exhibited a honeycomb-like crystal segregation. Metallographic and X-ray examinations indicate only slight variations of carbon concentration in the solid solution. A carbon content in the $\gamma$-phase higher than that corresponding to the E-point on the iron–carbon diagram cannot be obtained by quenching from the melt. The results suggest that the E-point lies at 1·7% carbon, not at 2·0% as assumed by some American publications.—J. P.

**The " Half " Double Equilibrium Diagram of the System Iron–Carbon and Its Relation to Ternary Alloys, Particularly Silicon.** E. Jänecke. (*Z. Metallkunde*, 1940, **32**, May, 142–144). The double diagram arises from considering cementite or graphite as being the stable phase. Evidence is collected to show that cementite decomposes at about 940° C. There is thus an invariant on the austenite solubility limit where austenite, graphite, and cementite are in equilibrium. Above 940° C. there is a simple equilibrium diagram with cementite, and below 940° C. the double diagram, with cementite as the unstable phases. This diagram is extended to the incongruent melting point of cementite at 1200° C. Applications to ternary systems such as Fe–C–Si shows the existence of regions for stable cementite and one for stable graphite separating from the melt.—K. G.

**Velocity of the Transformation from Partly Ordered to Ordered Atomic Distribution in $Fe_2NiAl$.** H. Hendus and E. Scheufele. (*Z. Metallkunde*, 1940, **32**, Aug., 275–277). An apparatus is described for measuring rates of change of resistivities at temperatures up to 700° C. Measurements were made on $Fe_2NiAl$ at 300–700° C. The changes in resistivity are found to be proportional to the degree of disorder and the theoretical predictions about the relation of the rate of transformation with temperature were confirmed. The activation energy for the process is 15 kg.cal./mole.—K. G.

**Study of the Martensite Transformation in Austenitic Irons.** P. Laurent and M. Batisse. (*Rev. Mét.*, 1952, **49**, Feb., 129–139). Three irons normally austenitic were studied by a dilatometric method. Martensite formation facilitates lower graphitization and, on heating, the martensite gives an austenite distinct from the initial phase. This suggests that the reaction is reversible as in copper–aluminium alloys.

**Thermodynamics of the Transformation of Martensite.** J. Manuel Pertierra. (*Tecn. Met.*, 1951, **7**, Nov.–Dec., 369–377). [In Spanish]. The general characteristics of the austenite–martensite transformation are discussed. Part of the thermodynamic calculations necessary for the determination of the decrease in free energy associated with the martensitic reaction are given. The variation in the free energy in

relation to temperature and carbon content is shown. A quantitative explanation of the transformations in the systems Fe–Ni and Fe–Mn is given by the application of thermodynamic principles to the equilibrium diagram.—R. S.

**Analytical Representation of Certain Phase Boundaries.** W. Rostoker. (*Trans. Amer. Inst. Min. Met. Eng.*; *J. Met.*, 1951, **3,** Dec., 1203–1205). Using an expression for the free energy of a homogeneous phase as a function of composition, the author derives a relationship for the phase boundaries extending from the allotropic transformation of the solvent metal. Comparisons between calculated and observed phase boundaries in the systems Fe–Ni, Fe–Mn, Fe–W, Ti–Mo, and Ti–Cb, are presented.—G. F.

**Formation of the Widmannstätten Structure in Iron–Nickel Meteorites.** U. Dehlinger. (*Z. Metallkunde*, 1940, **32,** June, 196–198). All evidence points to the conclusion that this structure represents the nearly final equilibrium condition in the binary phase between α and γ iron in the Fe–Ni diagram. It has therefore developed from the original martensite needles in the adjacent region. This is possible, since the martensite, owing to its own stresses and restricted separation, is not in complete equilibrium. The mechanism of the transformation is described. Thus, for the appearance of the structure in the meteorites, only slow cooling over a period of years of the iron–nickel alloys from the solidus to 100° C. is necessary.

**Influence of Cobalt on the Properties of Cementite.** A. Michel and J. Drain. (*Rev. Mét.*, 1952, **49,** Feb., 114–116). The thermal behaviour of carburized iron–cobalt alloys has been studied by thermomagnetic analysis to determine the effect of cobalt on the stability of iron carbide. The Curie point of the latter is raised from 210° to a maximum of 273° C.—A. G.

## CORROSION

**Semi-Accelerated Corrosion Tests of Medium and High Tensile Steel in Contact with Phenolic Foam.** H. J. Stark, J. Kaminetsky, and R. R. Winans. (*J. Amer. Soc. Naval Eng.*, 1952, **64,** Feb., 49–57). Contact with balsa wood and with three phenolic foams under alternate wet (salt water) and hot dry conditions is shown to cause slightly accelerated corrosion of mild and high-tensile steels. No correlation has been observed between the *p*H of the materials and their corrosive effects. Steel surfaces to be used under these conditions should receive a protective coating.—G. P. A.

**Wear in Friction Systems Caused by Electrochemical Transformations at Elevated Temperatures with Particular Reference to Ferrous Alloys.** H. Schiffers. (*Giesserei, Techn.-Wissensch. Beihefte*, No. 6–8, Mar., 1952, 395–401). The author reports on fretting corrosion studies of cast-iron stuffing boxes. Fretting corrosion always occurs when the ratio of redox-potentials differs from unity. Fretting corrosion intensifies mechanical wear. It is possible to adjust the potentials by alloy additions, and thus to reduce fretting corrosion. It appears, however, from subsequent tests *in situ* that not only the matching of redox potentials but the method of manufacturing the alloys are of importance.—J. G. W.

**Preventing Intergranular Corrosion Due to Welding Stainless.** S. C. Orr. (*Chem. Eng.*, 1952, **59,** Mar., 286–296). The parts played by the alloying elements in stainless steels are reviewed, and the three principal ways of preventing intergranular corrosion after welding are discussed. They involve either holding carbon to a minimum content, preventing carbide segregation by combining carbon with a stabilizing agent such as niobium or tantalum, or heat-treatment to dissolve the carbides, followed by rapid cooling. The last method is the most reliable.—T. E. D.

**A Contribution to the Knowledge of the Resistance to Attack by Sulphuric Acid of Alloys Low in Nickel Having a High Chromium Content with Additions of Molybdenum and Copper.** W. Tofaute and H. J. Rocha. (*Inst. Hierro y Acero*, 1952, **5,** Jan., *Special Issue*, 80–87). [In Spanish]. The mechanical properties, magnetic saturation, and resistance to $HNO_3$ and $H_2SO_4$ of some annealed alloys containing 20–30% Cr, 0–10% Ni, 0–3% Mo, and 0–3% Cu are examined. By adding 2% Mo and 1% Cu, alloys were obtained which, besides possessing good mechanical properties, have good passivity up to 50% $H_2SO_4$ at room temperature and up to 30% $H_2SO_4$ at 100° C. Resistance to $HNO_3$ depends largely on structure, the best alloys having exclusively austenitic or ferritic structures.

**Corrosion Processes on Galvanized and Chromized Iron.** E. Raub. (*Z. Metallkunde*, 1940, **32,** Apr., 105–108). The chromizing, with or without an intermediate layer of copper, brass or nickel, of galvanized iron to improve its appearance, reduces the protecting properties of the zinc layer. This is due to the setting-up of unsuitable galvanic couples. Only in good conducting solutions does the corrosion resistance remain. Non-porous chromium layers are recommended.

## ANALYSIS

**The Microchemical Analysis of Ferrous and Non-Ferrous Alloys.** G. W. C. Milner and W. R. Nall. (*Anal. Chim. Acta.*, 1952, **6,** May, 420–437). Methods for the absorptiometric determination of lead and vanadium in steels are described in detail.—T. E. D.

**Extraction of Cinchonine from Filtrate after Precipitation of Tungsten.** M. B. Zapadinskii. (*Zavodskaya Laboratoriya*, 1950, No. 1, 103). [In Russian]. A method is proposed for economy in the determination of tungsten by the recovery of the cinchonine used for precipitating its last traces.—S. K.

**On the Determination of Sulphur by the Combustion Method.** V. K. Chudinov. (*Zavodskaya Laboratoriya*, 1950, No. 1, 99). [In Russian]. Some improvements in the oxygen-combustion method for the determination of sulphur in ferrous metals are suggested. These include the addition of copper filings and calcined manganese dioxide to the sample in the boat, enabling combustion to be carried out at a considerably lower temperature.—S. K.

**A Stoichiometric Combustion Method for the Determination of Sulphur in Slags.** C. J. B. Fincham and F. D. Richardson. (*J. Iron Steel Inst.*, 1952, **172,** Sept., 53–55). [This issue].

**Determination of Combined Carbon in Graphitic Iron.** Methods of Analysis Committee. (*J. Iron Steel Inst.*, 1952, **172,** Sept., 79–86).] This issue].

**Calibration Standards for the Spectrographic Analysis of Two Components.** R. I. Knutzen. (*Z. Metallkunde*, 1944, **36,** Jan., 18–20). A method is described for the direct simultaneous determination of two components in a ternary alloy. It obviates calculations with relative concentrations.—K. G.

**Permanent Magnets for Spectrographs and Nuclear Physical Research.** D. Hadfield and D. L. Mawson. (*Brit. J. Appl. Phys.*, 1952, **3,** June, 199–202). The new anisotropic alloys can be made into composite permanent magnets which are independent of power supplies, and give a constant field. Flexibility is achieved in the electropermanent magnet either by reinforcing the field electromagnetically, or by artificially ageing the magnet to give a reduced field. Applications are discussed.—E. T. L.

**Spectrographic Analysis of Superficial Layers for the Protection of Metal Alloys—Application to Chromized Layers.** F. Malamand. (*Recherche Aéronautique*, 1951, July–Aug., 27–31). A method of surface spectrographic analysis combined with electrolytic polishing allows the study of the distribution of chromium in the diffusion zone after thermal chromizing. As many as 20 analyses in 0·1 mm. are possible.—T. E. D.

**Spectrum Analysis of Small Quantities of Nickel in Carbon Steels by the Visual Method.** M. N. Shtutman and V. I. Ivanov. (*Zavodskaya Laboratoriya*, 1950, No. 1, 45–47). [In Russian.] The method proposed is said to be satisfactory for the rapid determination, under works conditions, of residual nickel (down to 0·03%) in carbon steels.—S. K.

**Spectrophotometric Determination of Nickel in Steel.** M. D. Cooper. (*Analy. Chem.*, 1951, **23,** June, 875–880). The method, which is described in detail, gives good colour stability. The evaluation of the interference of copper and manganese is given. The ratios of these elements to nickel may be as high as 12·5 : 1 and 45 : 1 respectively, if special precautions are taken. Some analytical results and comparisons with other methods are quoted.—T. E. D.

**Influence of Complex Formation on the Value of the Potential of Systems Having Analytical Importance.** V. S. Syrokomskii and V. B. Avilov. (*Zavodskaya Laboratoriya*, 1950, No. 1, 11–16). [In Russian]. Ionic equilibria of iron, molybdenum, vanadium, and titanium, and the oxidation-reduction potentials of the corresponding systems are considered. The influence on the potential of the acidity of the solution and the presence of complex-forming ions is discussed.—S. K.

**Significance of Spectroscopic Analysis for Foundry Practice.** O. Werner. (*Giesserei*, 1952, **39,** Feb. 21, 73–81). The advantages of spectroscopic analysis in the foundry are discussed and equipment is described, followed by information on the installation in foundries, and calibration specimens.

The determination of magnesium in spheroidal cast iron is also described—J. G. W.

**Ultraviolet Spectrophotometric Determination of Vanadium.** G. Telep and D. F. Boltz. (*Analy. Chem.*, 1951, **23,** June, 901–905). The characteristic absorbency maxima of peroxyvanadic acid at 290 m$\mu$ and 460 m$\mu$ are used. Interfering ions are mentioned, but the procedure developed is satisfactory for determining 0–125 p.p.m. of vanadium.—T. E. D.

**Rapid Photometric Determination of Aluminium in Zinc and Steel.** L. C. Ikenberry and A. Thomas. (*Analy. Chem.*, 1951, **23,** Dec., 1806–1809). This method is based on the reaction of aluminium with eriochromecyanin *R* to form a violet-red complex. The reproducibility equals that of gravimetric methods, with great saving of time. It may be used for aluminium concentrations of 0·002–0·1%.—T. E. D.

**The Identification of Metals and Alloys by Chemical Spot Testing.** C. T. Wilshaw. (*Metallurgia*, 1952, **45,** Feb., 102–106). A spot-testing procedure, using a small number of simple reagents, has been developed for the identification of alloys rather than of a particular element. The scheme covers ferrous alloys and those non-ferrous alloys not readily distinguished from them by density or colour.—T. E. D.

**Observations on the Sampling of Ferro-Alloys.** M. D. E. Jonckers. (*Chim. Analy.*, 1952, **34,** Apr., 75–82). Composition variation within ingots and within varying sizes of particles makes sampling procedures very important. Procedures are suggested for obtaining bulk and small samples, with particular reference to Fe–P, Fe–Si, Fe–C–Ti, and Fe–Mn. Contamination during sample preparation is mentioned.—T. E. D.

**The Method Used in the Murex Laboratories for the Determination of Silicon, Chromium and Iron in Ferro-Chromium.** E. A. Chidley. (*Murex Review*, 1952, **1,** 10, 239–240). The method, using ammonium molybdate, stannous chloride, and sulphuric acid is described in detail.—J. P. S.

**Application of Physico-Chemical Methods of Metallography to the Mineralogical Analysis of Iron Ores.** A. Portevin. (*Inst. Hierro y Acero*, 1952, **5,** Jan.–Mar., 215–220). [In Spanish]. The author refers briefly to work carried out at the Institut de Recherches de la Sidérurgie on some French ores. The following tests were made: Differential thermal analyses; crystallographic and microscopic examination; chemical and thermomagnetic analyses is given.—R. S.

## HISTORICAL

**From the Editor's Viewpoint.** V. C. Faulkner. (*Foundry Trade J.*, 1952, **92,** Mar. 15, 9–16). In the jubilee issue of this journal, the editor reviews the changes in the industry since its beginning.—E. T. L.

**500 Years Ironfounding Crammed into 50 Years.** J. J. Sheehan. (*Foundry Trade J.*, 1952, **92,** Mar. 15, 17–22). In the last 50 years progress has been as great as in the previous 500 years of ironfounding. The author traces the technical advances, including sand practice, cupola practice, moulding sands, and dissemination of knowledge.—E. T. L.

**50 Years Evolution of the Equipment Industry.** J. Blakiston. (*Foundry Trade J.*, 1952, **92,** Mar. 15, 23–33). This is an illustrated history of the mechanization of ironfounding.

**50 Years Pipe-Dreams to Practice Through Cast-Iron Research.** J. G. Pearce. (*Foundry Trade J.*, 1952, **92,** Mar. 15, 57–64). The author outlines advances coming from research in the last 50 years. The improvements mentioned include the reduction of carbon content, the process of silicon inoculation, the addition of alloy metals, heat-treatment, centrifugal casting, nodular cast iron, measurement of sand properties, shell-moulding, hot-blast cupolas, and testing.—E. T. L.

**America Outstripped in 50 Years of Malleable Iron.** F. D. Ley. (*Foundry Trade J.*, 1952, **92,** Mar. 15, 73–80). This review deals with pulverized fuel, moulding machines, fettling, annealing, furnace design, controlled-atmosphere furnaces, straightening, and working conditions.—E. T. L.

**Neath Abbey Iron Works—19th Century Founding.** T. R. Harris. (*Foundry Trade J.*, 1952, **92,** Mar. 15, 87). The author quotes from old papers concerning the operation of the Neath Abbey ironworks.—E. T. L.

**Samuel Osborn's of Sheffield: Centenary of World-Famous Steel Company.** (*Brit. Steelmaker*, 1952, **18,** Apr., 174–178). The present year is the centenary of the Sheffield firm of Samuel Osborn and Co., Ltd. This article describes the development of the firm from the small file-manufacturing plant to the present-day company which controls five large works in Sheffield alone.—G. F.

**Robert Forester Mushet: Discovery of Self-Hardening Tool Steel.** F. M. Osborn. (*Brit. Steelmaker*, 1952, **18,** Apr., 180–185). This article is an extract from the author's book "The Story of the Mushets"; it describes Robert Forester Mushet's discovery of self-hardening tool steel and the arrangements made with Samuel Osborn and Co., Ltd., for its manufacture.

**A Century of Tool Steel Development.** E. N. Simons. (*Brit. Steelmaker*, 1952, **18,** Apr., 186–193, 195). The author discusses the evolution of the tool-steel industry in the last 100 years, and describes the contributions of Mushet, Sorby, Roberts-Austen, Brinell, and Taylor.—G. F.

**Early Ironmasters in South Wales.** F. Evans. (*Brit. Steelmaker*, 1952, **18,** Mar., 115–121, 135). The author outlines the development of the iron industry in South Wales during the 18th and 19th centuries, and discusses the achievements of the early ironmasters, including Anthony Bacon, the Homfray brothers, John Guest, and Richard Crawshay and his descendants.—G. F.

**The History of Flow Measurement by Differential Pressure. I—The Work of Venturi.** (*Instrument Engineer*, 1952, **1,** Apr., 18–19). This is the first of a series of articles designed to trace the history of the discovery and application of the principle of differential pressure. A short biography of Giovanni Battista Venturi is given.—J. P. S.

## ECONOMICS AND STATISTICS

**The World's Steel Industry Under Stress.** W. Salewski. (*Stahl u. Eisen*, 1952, **72,** Apr. 24, 453–459). The problems confronting the world's steel industry in maintaining production and balance between types of steel in face of rearmament, investment, and civilian demands and raw material shortages are reviewed.—J. P.

**Stainless Steel in War Time.** C. M. Lerici. (*Acciaio Inossid.*, 1952, **19,** Mar.–Apr., 31–33). [In Italian]. The author discusses European production of stainless steels with special reference to the manufacture of chromium steels and chromium–manganese steels. There is a very serious discrepancy in cost of stainless steels in producer and non-producer countries., which imposes a heavy handicap on the latter.—M. D. J. B.

**French Iron and Steel Industry: Post-War Recovery and Development Plans Outlined.** M. Moyal. (*Brit. Steelmaker*, 1952, **18,** Jan., 16–18, 21). The author discusses the post-war recovery of the French iron and steel industry, which virtually ceased to exist due to war-time devastation. The country is now the fifth largest steel producer in the world, and is the largest exporter of steel products. The industry's development plans are outlined.—G. F.

**Italian Iron and Steel Industry in 1951.** G. Coppa-Zuccari. (*Australian Found. Trade J.*, 1952, **3,** Feb., 5). Statistics are quoted which show that the present Italian production of iron and steel exceeds the pre-war level by nearly 25%. Present production is about 955,000 tons of cast iron and 2,950,000 tons of steel annually.—P. M. C.

**Mining and Ferrous Industry Development in Latin America.** (*Echo Mines*, 1952, Apr., 251–252). The needs of Latin America for assuring its development, and the exploitation of mineral resources are surveyed. The iron and steel industries are mentioned and reference is made to expansion projects.—T. E. D.

**Steel Developments in Rumania: Extensive Long-Term Programme.** (*Iron Coal Trades Rev.*, 1952, **164,** Apr. 11, 829–831). Brief descriptions are given of the major steelworks in Rumania and of their sources of raw materials supplies. The country plans to expand its annual steel production from the current 500,000 tons to 1,250,000 tons by 1955.—G. F.

## MISCELLANEOUS

**Heat and Work.** T. Bedford. (*Research*, 1952, **5,** Apr., 155–162). Some of the investigations that have been carried out to determine the influence of temperature on the efficiency and health of industrial workers are reviewed. These show that the rate of production, and the well-being of workers, are markedly affected by the temperature of the working place.—C. J. B. F.

**Heat Relief in Industry.** B. R. Small. (*Iron Steel Eng.*, 1952, **29,** Apr., 71–77). This article describes a number of methods of providing heat relief in industry and so improving

working conditions. Ventilation and spot cooling in mill buildings are also considered.—M. D. J. B.

**Work in Metal Plants Made More Agreeable by Ventilation.** L. Oppl. (*Hutník* (Prague), 1952, **2,** Mar., 58–61). [In Czech]. Correct ways of ventilating metal-working plants, rolling mills, and foundries by natural draught and by fans are considered.—P. F.

**Handling and Lifting—Their Hazards and Prevention.** A. Taylor. (*Foundry Trade J.*, 1952, **92,** Mar. 27, 337–339). Almost half of the notifiable accidents occur during lifting and handling, and the total cost of an accident is about five times the compensation cost. The author deals with accidents in lifts and with cranes, particularly chain slings, wire ropes, and cut-out switches.—E. T. L.

**The Human Approach to Safety in the Chemical Laboratory, Workshop, and Plant.** L. J. Burrage. (*Research*, 1952, **5,** Feb., 62–66).

**Noteworthy Accident Risks in Steelworks.** G. Zweiling. (*Stahl u. Eisen* 1952. **72,** Apr. 24, 502–508). There are many sources of accident in a steelworks and minor incidents may often have major effects. Some of these sources are described. The need for ' safety consciousness ' on every worker's part is stressed.—J. P.

**Training and Welfare at Thorncliffe.** (*Engineer*, 1952, **193,** Apr. 11, 502). **Welfare at Thorncliffe.** (*Iron Steel*, 1952, **25,** May, 163–164). This article describes the recently opened foundry baths and extension to the apprentice training school at the works of Newton Chambers and Co., Ltd.—M. D. J. B.

**Relation Between the Research Worker and the Practical Steelmaker: Need for Understanding and Co-operation.** A. H. Leckie. (*Iron Coal Trades Rev.*, 1952, **164,** Apr. 4, 745–749). The author critically examines the relation between the research worker and the practical steelmaker. He indicates the potentialities and limitations of research workers and shows how the best co-operation with industrial production personnel can be maintained.—G. F.

**Industrial High Vacuum and Its Application to Some Metallurgical Problems.** J. P. Baxter. (Australian Inst. Metals: *Australasian Eng.*, 1952, Feb. 7, 76–79). The author discusses in general terms the engineer's problems in the production of high-vacuum plant. The several types of vacuum measuring gauge are also briefly described.—P. M. C.

**Use of Models in Research: Theoretical Aspects of Similitude.** M. D. J. Brisby. (*Iron Coal Trades Rev.*, 1952, **164,** Apr. 11, 825–827, 831). The author discusses the value of model work and describes the theoretical aspects of similitude which must be taken into account before comparing models and full-scale installations. Geometric, kinematic, and dynamic similitude are considered separately, and a simple example is quoted.

**Steelworks Maintenance: Organization at Appleby-Frodingham.** K. Paterson. (*Iron Steel*, 1952, **25,** Feb., 39–45). The author discusses the maintenance organization at the Appleby-Frodingham Steel Company. After briefly describing the layout of the works, he describes in detail the work of the mechanical, electrical, civil, and road transport engineers' departments, and of the central engineering workshops.—G. F.

**New Thermodynamic Concepts Bring Theory and Practice into Agreement.** N. P. Bailey. (*Chem. Eng.*, 1952, **59,** Mar., 150–154). Hitherto undetected fallacies in classical thermodynamics are revealed, and the new approach, treated briefly in this article, explains the discrepancies between theory and practice found in flow problems.—T. E. D.

**Convenient Flowmeter Conversions.** D. P. Herron. (*Chem. Eng.*, 1952, **59,** Mar., 142–143). A single relation is deduced which enables all types of differential-pressure flowmeters to be calibrated with any fluid and the calibration converted to any other fluid without loss of accuracy. The expression is valid in both the streamline and turbulent regions, and experimental data are quoted as proof of its applicability even for relatively great differences in the densities and viscosities of the fluids flowing.—T. E. D.

**Use of Radioactive Isotopes in Industry.** (*Min. J.*, 1952, **238,** May, 473–474). A general review of the application of the technique is made. (13 references).—B. G. B.

# BOOK NOTICES

CHAMPION, F. A. "*Corrosion Testing Procedures.*" 8vo, pp. xi + 369. Illustrated. London, 1952: Chapman and Hall, Ltd. (Price 36*s.*)

This book describes the procedures adopted by investigators of many diverse types of corrosion, discussing the factors which must be considered if dependable results are to be obtained. Attention is directed mainly to studies at ordinary or slightly elevated temperatures of the corrosion of metals and metallic coatings, less to organic coatings. The size, identification, and methods of preparing specimens, including the application of coatings, are dealt with first, then the environments to which they are to be exposed. Exposure conditions in the laboratory, both under simple conditions and under conditions of conjoint action, and in the field or in service are described in detail, factors of importance under the various conditions being listed. Methods of cleaning specimens after corrosion are given in a short chapter, and the assessment of effects of corrosion on the metal and on the environment are discussed fully. The book concludes with brief accounts of ancillary observations, special tests, and the expression and interpretation of results.

The methods described cover the types of metals and exposure conditions likely to be met with in corrosion testing, and there are numerous references to the literature. The book should enable those undertaking this kind of work for the first time to proceed with confidence, and it may be hoped that more university students will be encouraged to study corrosion as a post-graduate research project. The final chapter on the expression and interpretation of results could well have been more detailed, particularly as regards statistical methods and the recording and application of results; in the past, engineers and architects have sometimes been slow to make use of the results of corrosion tests, because scientific workers have not always reported their work in the most suitable manner.

T. A. BANFIELD

MATTHAES, KURT. "*Die Prüfung metallischer Werkstoffe.*" 8vo, pp. 210. Illustrated. Berlin-Grunewald, 1952: Metall-Verlag G.m.b.H. (Price DM 15.–)

The testing of materials has been developed to show up differences between different materials which will enable a correct assessment to be made of their relative values for the purpose for which they are to be used. It is therefore only possible to judge the suitability of a particular method of test in the light of the properties required for that purpose. The author has attempted, within the compass of a small book, to cover briefly the whole field of mechanical testing of metallic materials, with the particular object of drawing attention to the way in which the methods of test are related to the properties of the material which the tests are designed to measure. Accordingly, such features of the usual books on this subject as descriptions of testing machines and equipment are reduced to a bare minimum, in favour of fuller information on the effects of the conditions of the test on the results obtained. A further consequence of the author's method of treatment is that space is mainly devoted to those tests on which considerable research has been carried out, particularly in Germany in recent years, while those tests which have not received such concentrated study are dismissed in a few paragraphs—in some cases more briefly than their importance merits.

The book is divided into six sections. Section I deals with static tests on metals. Nearly half of it is devoted to the tensile test, and hardness testing is discussed in some detail, but other forms of static test, such as compression, bending, and torsion tests, are dealt with only very briefly. Section II contains very short descriptions of tests for sheet metal, wires, and tubes.

Section III, on testing under dynamic stresses, deals reasonably fully with notched-bar impact testing and fatigue testing, and refers very briefly to tests for wear and machinability.

The first part of Section IV deals with the effect of temperature on the properties of metals and refers particularly to creep testing. The second part of this section deals with corrosion testing, and includes discussions on erosion by water and on stress corrosion, but excludes corrosion fatigue, which receives only a very brief mention in the section on fatigue testing.

Non-destructive methods of test form the main subject of Section V, which deals with methods of distinguishing between materials (other than by chemical and metallurgical methods) and of detecting defective materials.

Crack detection and testing by sonic and ultrasonic, X-ray and gamma-ray, and magnetic and electric methods are discussed.

The final Section VI discusses acceptance testing and its organization at the user's works.

The book has the merit of being up-to-date, at least so far as German work is concerned, and a full bibliography, to which frequent reference is made in the text, is appended. From the point of view of the British reader, however, it suffers from two drawbacks: The details of tests refer almost exclusively, as might be expected, to the DIN standard tests; and neither the text nor the bibliography appears to have taken sufficient account of the more recent British and American work on the subject.—H. R. Mills

## NEW PUBLICATIONS

Anglo-American Council on Productivity. "*Iron and Steel.*" 4to, pp. xii + 147. Illustrated. London, 1952: The Council. (Price 5*s.*)

Anglo-American Council on Productivity. "*Steel Construction.*" 4to, pp. viii + 70. Illustrated. London, 1952: The Council. (Price 3*s.*)

"*ASTM Specifications for Steel Piping Materials. Pipe, Tubes, Castings, Forgings, Bolting.*" Prepared by ASTM Committee A-1 on Steel. 8vo, pp. x + 372. Philadelphia, 1952: American Society for Testing Materials. (Price $3.50)

Ballay, M., J. Bénard, G. Chaudron, J. Duflot, P. Lacombe, and A. Portevin. "*Introduction à l'Etude de la Corrosion Métallique dans les Industries Pétrolières et Chimiques.*" Ouvrage publié avec le concours de l'Institut français du Pétrole. La 8vo, pp. 220. Illustrated. Paris, 1952: Société d'Edition d'Enseignement superieur. (Price 1750 fr.)

Brailsford, F. "*Magnetic Materials.*" Second edition, revised. Sm. 8vo, pp. ix + 156. Illustrated. London, 1951: Methuen and Co., Ltd.; New York: John Wiley and Sons, Inc. (Price $1.50)

British Iron and Steel Federation. "*Statistics of the Iron and Steel Industry of the United Kingdom for* 1951." La. 4to, pp. vii + 119. Illustrated. London, 1951: The Federation. (Price 7*s.* 6*d.*)

British Standards Institution. B.S. 501, 554: 1952. "*Reports on Metric Units of Volume and Standard Temperature of Volumetric Glassware.*" 8vo, pp. 16. London, 1952: The Institution. (Price 2*s.* 6*d.*)

British Standards Institution. B.S. 612: 1952. "*Nessler Cylinders.*" 8vo, pp. 10. Illustrated. London, 1952: The Institution. (Price 2*s.*)

British Standards Institution. B.S. 1121: Part 24: 1952. "*Methods for the Analysis of Iron and Steel.*" Part 24. "*Small Amounts of Chromium in Iron and Steel (Absorptiometric method).*" 8vo, pp. 7. London, 1952: The Institution. (Price 2*s.*)

British Standards Institution. B.S. 1210: 1952. "*Wood Screws.*" 8vo, pp. 24. Illustrated. London, 1952: The Institution. (Price 3*s.*)

Bush, N. L. "*Art and Science of Founding.*" Pp. 333. Illustrated. Sydney, Australia, 1951: Angus and Robertson, Ltd. (Price 40*s.*)

Clauser, H. R. "*Practical Radiography for Industry.*" La. 8vo, pp. x + 301. Illustrated. New York, 1952: Reinhold Publishing Corporation. (Price 60*s.*)

Conn, G. K. T., and F. J. Bradshaw. "*Polarized Light in Metallography.*" 8vo, pp. xi + 130. Illustrated. London, 1952: Butterworth's Scientific Publications. (Price 21*s.*)

Cords, Erich. "*Die technische Entwicklung des Peiner Walzwerks* 1872–1950." 8vo, pp. 115. Illustrated. Düsseldorf, 1952: Verlag Stahleisen m.b.H. (Price DM. 8.–)

Freeman, H. G. "*Fachwörterbuch Werkzeuge.*" Part II English–German. Sm. 8vo, pp. 390. Essen, 1952: Verlag W. Girardet. (Price DM. 24.–)

"*Gmelins Handbuch der anorganischen Chemie.*" 8. völlig neu bearb. Aufl. System-Nr. 17: "*Arsen.*" 8vo, pp. xv + 475. Illustrated. Weinheim/Bergstrasse, 1952: Verlag Chemie, G.m.b.H. (Price DM 140.–)

"*Gmelins Handbuch der anorganischen Chemie.*" 8. Aufl. System-Nr. 27: "*Magnesium.*" T.A. Lfg 4. "*Legierungen von Magnesium mit Zinc bis Rhenium. Oberflächenbehandlung.*" 8vo, pp. 483–818. Illustrated. Weinheim/Bergstrasse, 1952: Verlag Chemie, G.m.b.H. (Price DM 100.–)

Institut International de Physique Solvay. "*L'Etat Solide.*" Neuvième Conseil de Physique tenu à l'Université Libre de Bruxelles du 25 au 29 septembre, 1951. Rapports et discussions publiés par les Secrétaires du Conseil sous les auspices de la Commission Administrative de l'Institut. 8vo, pp. 580. Illustrated. Bruxelles, 1952: R. Stoops, Editeur. (Price: paper cover 650 fr.; bound 725 fr.)

Institute of Metals. "*The Cold Working of Non-Ferrous Metals and Alloys.*" A Symposium on metallurgical aspects of the subject held in London on the occasion of the Annual General Meeting of the Institute, 14 March 1951. Institute of Metals Monograph and Report Series No. 12. 8vo, pp. 207. Illustrated. London, 1952: The Institute. (Price 15*s.*)

Jessop, H. T., and F. C. Harris. "*Photoélasticité, Principes et Méthodes.*" Traduit par G. Henriot. La. 8vo, pp. vii + 236. Illustrated. Paris, 1952: Dunod. (Price 2350 fr.)

Loehr, Maja. "*Thörl.*" Geschichte eines steirischen Eisenwerkes vom vierzehnten Jahrhundert bis zur Gegenwart. 8vo, pp. viii + 176. Illustrated. Vienna, 1952: Verlag für Geschichte und Politik. (Price 80 schilling).

Mallick, R. W., and A. T. Gaudreau. "*Plant Layout Planning and Practice.*" Pp. 391. Illustrated. New York, 1951: John Wiley and Sons, Inc. (Price $7.50)

Mayer, Karl. "*Was der Siemens-Martin-Stahlwerker von seiner Arbeit wissen muss!*" (Stahleisen-Schriften. H.3.) 8vo, pp. 151. Illustrated. Düsseldorf, 1952: Verlag Stahleisen m.b.H. (Price DM 8.50)

National Bureau of Standards. "*Mechanical Properties of Metals at Low Temperatures.*" Proceedings of the NBS Semicentennial Symposium on Mechanical Properties of Metals at Low Temperatures. Held at the NBS on May 14 and 15, 1951. 8vo, pp. iv + 206. Washington, 1952: U.S. Government Printing Office. (Price $1.50)

Organisation for European Economic Co-operation. "*Documentation Techniques in the USA.*" 8vo, pp. 57. Paris, 1951: Organisation for European Economic Co-operation. (Price 4*s.*)

Pawlek, Franz. "*Magnetische Werkstoffe.*" (Reine und angewandte Metallkunde in Einzeldarstellungen. 13.) 8vo, pp. vii + 303. Illustrated. Berlin, Göttingen, Heidelberg, 1952: Springer-Verlag. (Price DM. 42.–)

Ernst, Richard. "*Deutsch-englisches, englisch-deutsches technisches Wörterbuch,*" in zwei Banden. Bd. II. "*English-deutsch.*" Pp. 669. Wiesbaden, 1951: Brandstetter Verlag, vorm. Tauchnitz Edition. (Price DM 19.80)

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Society of Automotive Engineers. "1952 *S.A.E. Handbook.*" La. 8vo, pp. 946. Illustrated. New York, 1952: The Society. (Price $6, special Library rate).

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"*The Welding Review Year Book* 1952." General Editor, J. V. Brittain. 8vo, pp. 309. Illustrated. London, 1952: Engineering Trades, Ltd. (Price 9*s.* 6*d.*)

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Wyckoff, H. O., and Lauriston S. Taylor. "*X-Ray Protection Design.*" National Bureau of Standards Handbook 50. 8vo, pp. iv + 36. Washington, 1952: U.S. Government Printing Office. (Price 15 cents).

Youden, W. J. "*Statistical Methods for Chemists.*" Pp. x + 126. Illustrated. New York, 1951: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price 24*s.*)

## ERIC WINEARLS COLBECK, M.A., F.I.M.

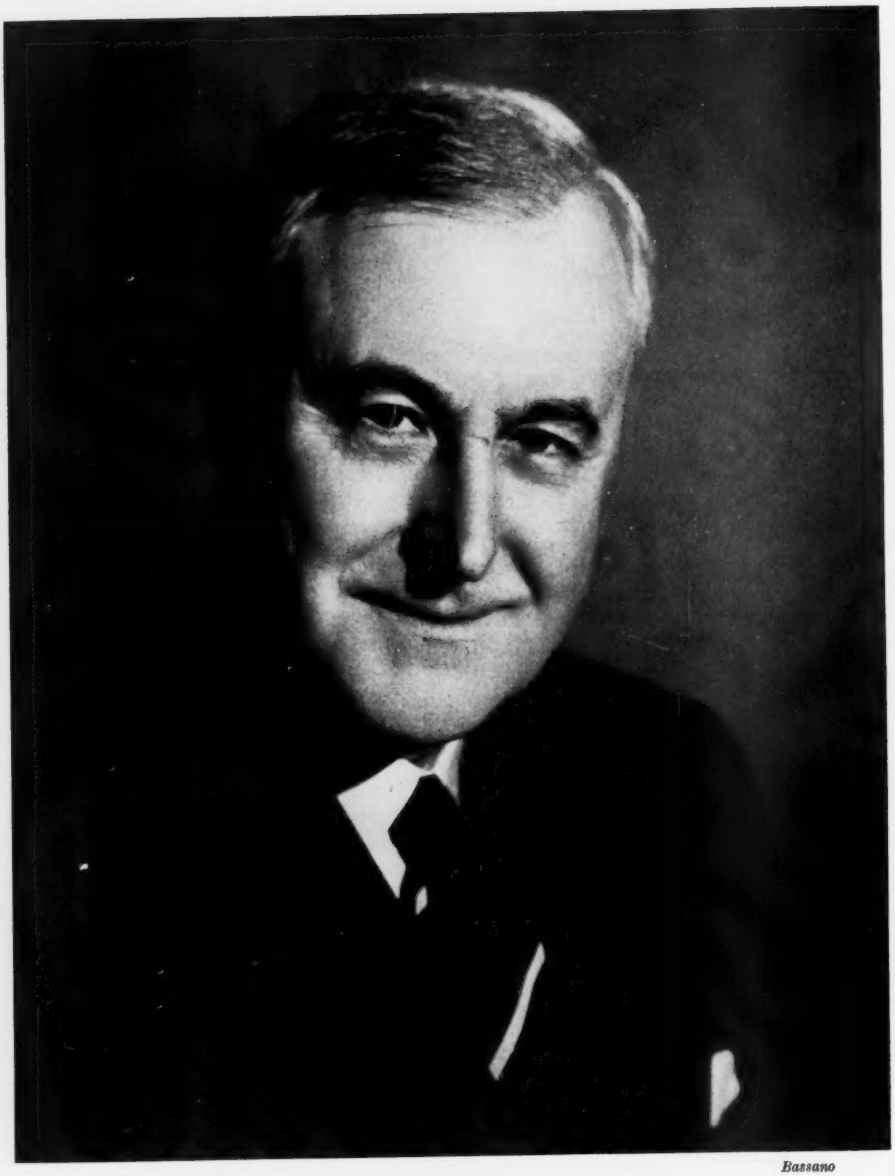
ERIC WINEARLS COLBECK was born in London in 1899. He was educated at Rugby School, and on leaving in January, 1918, became an Officer in The Special Brigade, Royal Engineers; he went out to France with the B.E.F. in September of that year. After finishing his Military Service in 1920, he entered Gonville and Caius College, Cambridge, taking the Mechanical Sciences Tripos. He graduated with Honours in 1922, with special distinction in Engineering Chemistry.

After graduation Mr. Colbeck commenced his metallurgical career as a Junior Scientific Officer in the Metallurgy Department of the National Physical Laboratory, under Dr. Walter Rosenhain. In 1924 he was appointed Technical Assistant to the General Manager of the Openshaw Works of Messrs. Sir W. G. Armstrong Whitworth and Company, Manchester, where he remained for four years. He took his M.A. in 1927.

In 1928 Mr. Colbeck joined the Research Department of the Alkali Division of Imperial Chemical Industries, Limited, Northwich, Cheshire, becoming Chief Metallurgist to this Division and Consulting Metallurgist to several other Divisions during the period 1928–1947. From 1945 to 1946 he was seconded to the Department of Atomic Energy, Ministry of Supply, as Metallurgical Advisor to the Director of Research (Sir John D. Cockcroft) and the Controller of Production (Lord Portal). During this period he was Chairman of the Metallurgical Committee dealing with Uranium Metal Production. He returned to the heavy steel industry in 1947 on his appointment as Metallurgical and Research Director to the Hadfield Group of Companies, of which he is also the Director in Charge of Hadfields Steels Limited, and a Director of Hadfields Forgings Limited.

He is the author of a large number of papers on a wide variety of metallurgical subjects; his first paper to The Iron and Steel Institute was given as long ago as 1924. He is also a Moulton Medallist of the Institution of Chemical Engineers, for his papers on the low-temperature properties of ferrous and non-ferrous materials.

Mr. Colbeck is a Past-President of the Institution of Metallurgists, of which he is a Founder Fellow, and also of the Manchester Metallurgical Society. He has been elected President of the Sheffield Metallurgical Association for 1952. He is a member of several Metallurgical Committees, including the Council of the British Iron and Steel Research Association and also the Inter-Services Metallurgical Research Council, of which he is Chairman of the Ferrous Metals Committee. He is Chairman of the Metals Advisory Committee and a member of the Harwell Power Committee of the Department of Atomic Energy. In 1951 he was elected a Freeman of the Cutlers' Company in Hallamshire. Mr. Colbeck has been a Member of The Iron and Steel Institute since 1924 and is a member of the Institute of Metals and other British and American Metallurgical Societies.



*Bassano*

**E. W. Colbeck, M.A., F.I.M.**

**Honorary Member of Council, 1952**